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BUREAU of SOLID WASTE DISPOSAL
December 1982

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Analysis of Operation and Emissions from Typical Hazardous Waste Treatment Processes

December 3, 1982

Commonwealth of Massachusetts

Department of Environmental Management

Bureau of Solid Waste Disposal

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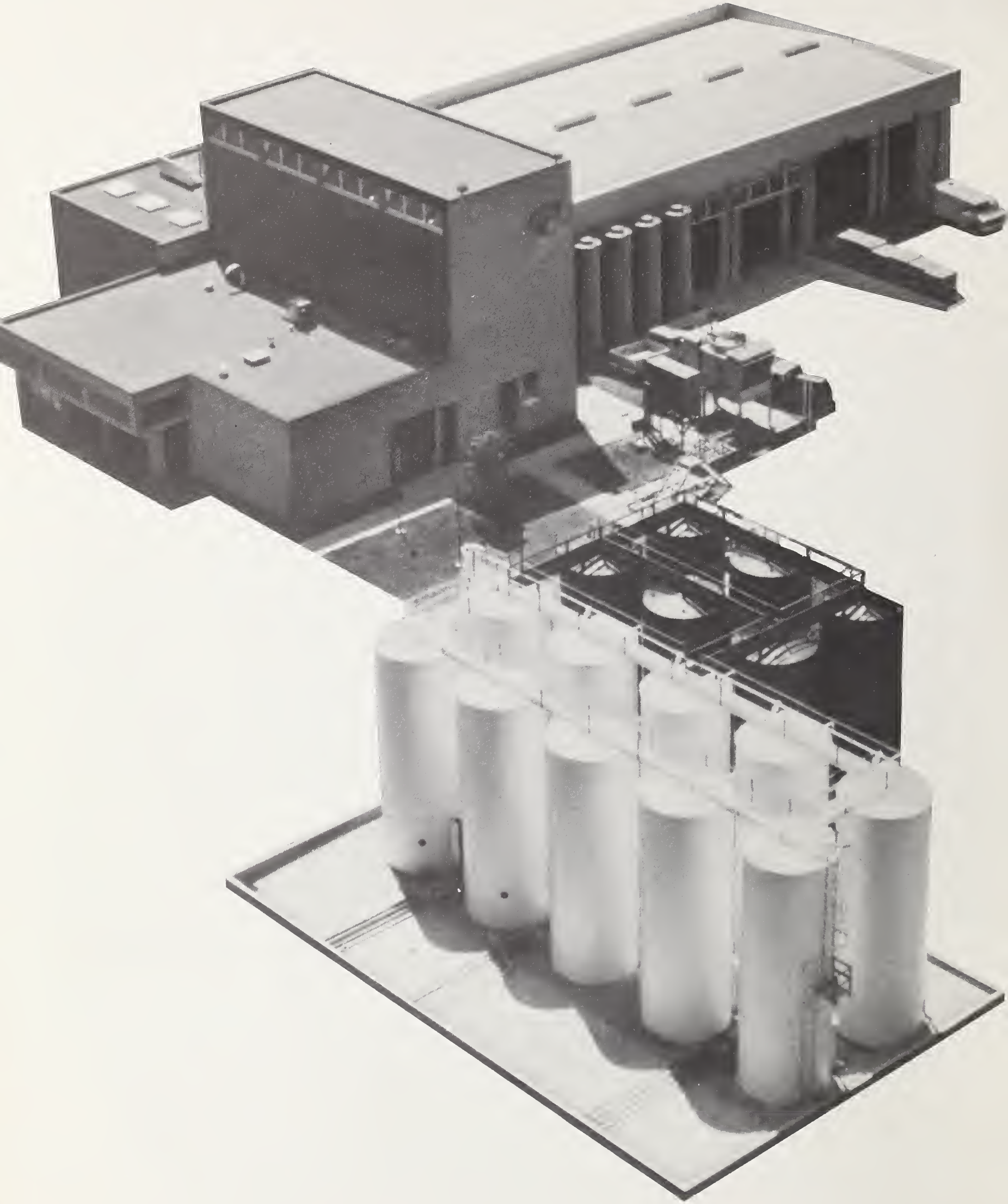
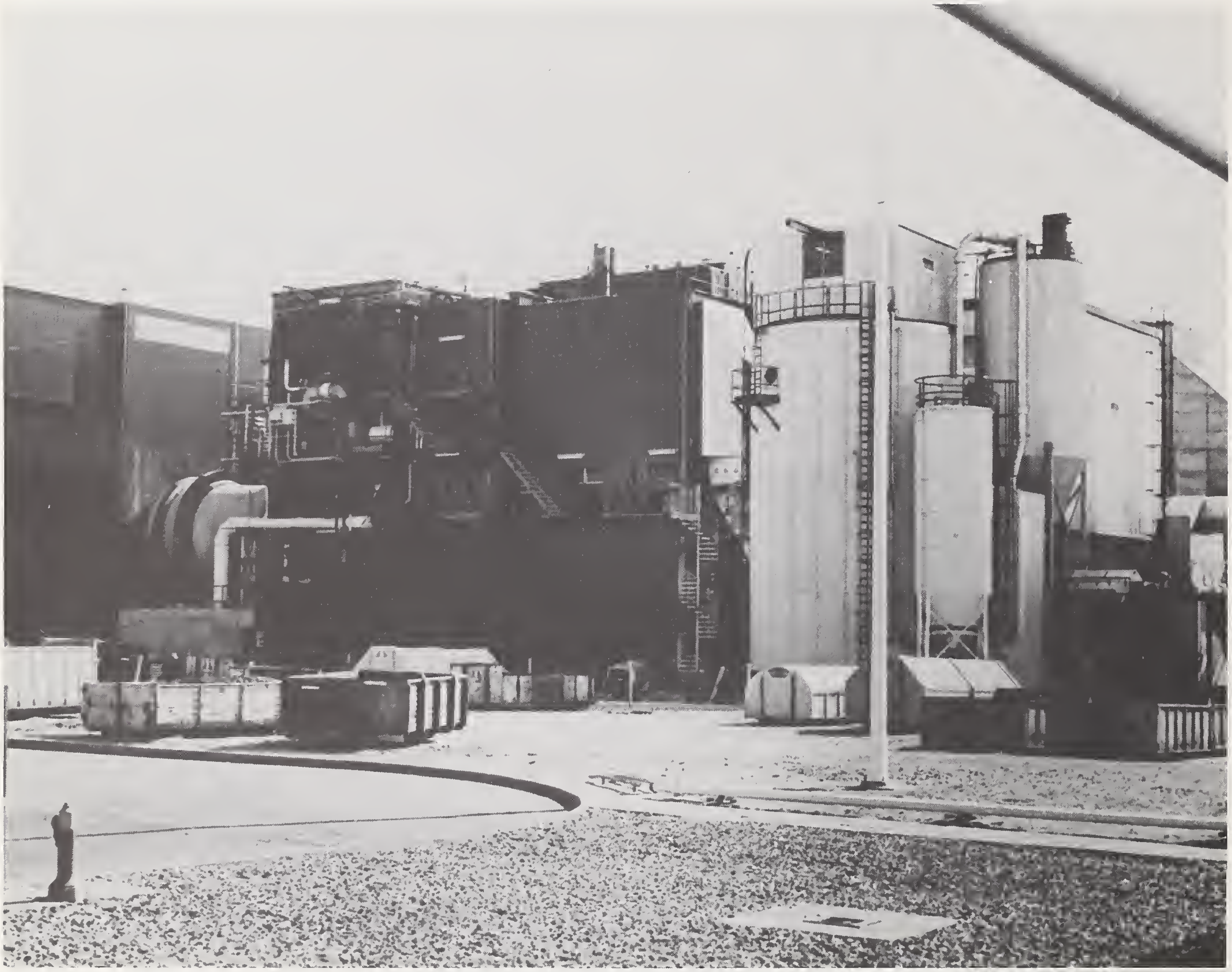


SOLVENT RECOVERY PLANT

INSIDE AN AQUEOUS WASTE TREATMENT PLANT



ROTARY KILN INCINERATOR

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1. INTRODUCTION

1. INTRODUCTION

This report has been prepared on behalf of the Department of Environmental Management of the Commonwealth of Massachusetts to assist citizens in understanding the consequences resulting from the operation of one type of hazardous waste disposal facility. Those components or treatments which will typically be used are described. There are so many possible treatments that not all can be described. The subjects that are discussed are:

Incineration of Combustible Waste

Recovery of Solvents

Wastewater Treatment (Aqueous Waste Treatment)

Chemical Fixation and Disposal of Non-Combustible Solids

Emission of Heat and Consumption of Water

The treatments are illustrated in Figure 1-1.

We hope that this report will enable local authorities to ask facility developers the best questions, to obtain necessary guarantees and protection, and to conduct their own approval and monitoring procedures.

Recommendations are given following each technical section and the reader is referred to SECTION 2.5 for recommendations on transport, to SECTION 5.9 for recommendations on monitoring and control of the incinerator, to SECTION 7.14 for recommendations on disposal of treated wastewater, to SECTION 8.4 for recommendations for disposal of non-combustible solids and to SECTION 9.4 for recommendations on steam released from the stack.

1.1 Terminology

Throughout this report, emphasis is placed on emissions and the consequence of failure. These subjects are considered separately for each treatment. It is important that their meaning be understood. It is also useful to draw distinctions between release, discharge and disposal. These words are not always given distinct meanings but have been given distinct meanings in this report.

A hazardous waste treatment facility cannot destroy matter. It merely changes the form. For every pound weight of waste, fuel, air and

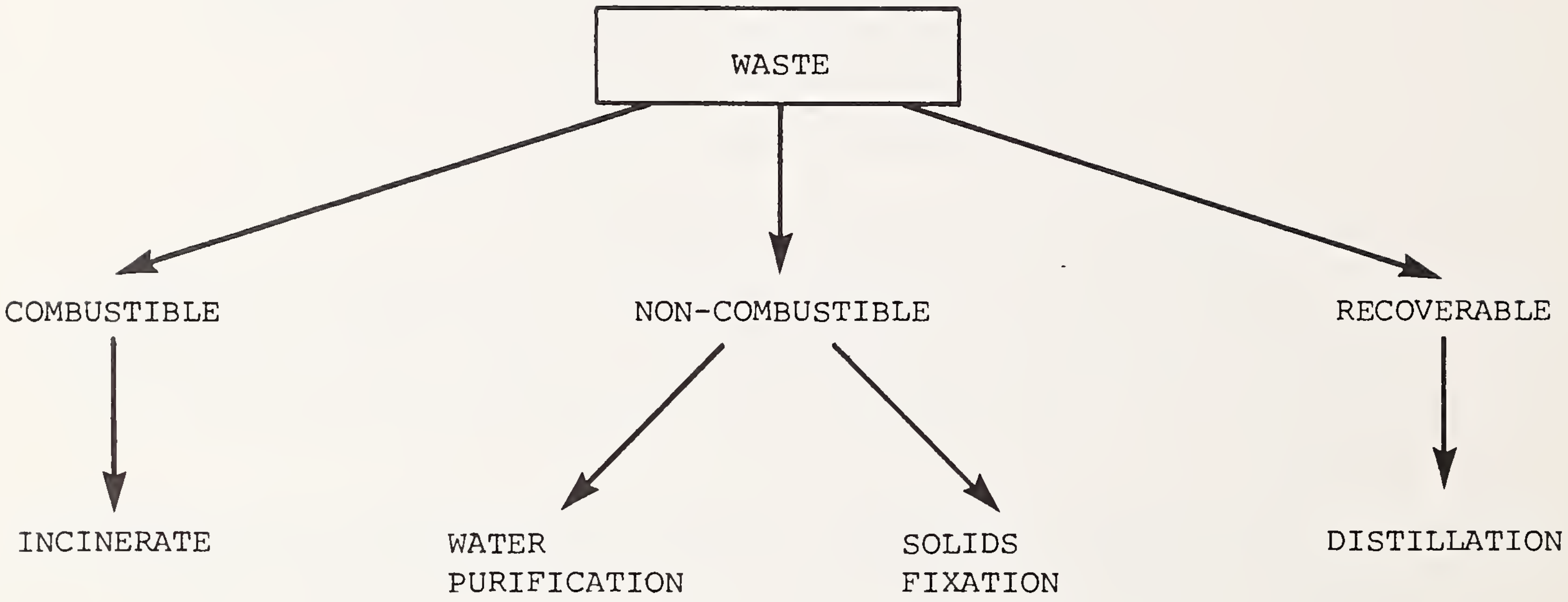

Figure 1-1. Treatments discussed.

water put into the facility, one pound weight of material leaves, or is emitted from, the facility. The weight of total emissions equals the weight of total input to the facility. Emissions can be conveniently classified as:

Vapors or Gases
Liquids that are not water
Water
Solids
Sludges

A sludge is a mixture of solid and liquid with a high proportion of solid.

The largest weight of emissions from an incinerator will be gases. By far the largest weight of gas will be nitrogen (derived from the air), water vapor (derived from evaporating wastewater and burning waste and fuel), carbon dioxide (derived from burning waste and fuel) and oxygen (derived from the air). These gases are nontoxic, odorless and colorless.

Gas emissions are released to the atmosphere. Vapors and gases are cleaned to remove hazardous compounds, passed up a tall stack and released. The vapors and gases from the tall stack are distributed widely in the atmosphere and diluted by the atmosphere. Vapors and gases must be monitored to ensure that excessive hazardous compounds are not released. If excessive hazardous compounds are detected, emission must be stopped. The consequence of failure of treatment, or gas cleaning, must be to stop emitting. Fortunately, emission of gases and vapors can be stopped quickly (in a few minutes). Vapors are emitted because liquid is being heated or boiled. If the heat supply is stopped, emission stops soon afterwards. Gases are emitted from an incinerator. If fuel and air are stopped, incineration stops very quickly.

Liquids that are not water will leave the facility only if someone has a use for them. Otherwise they must be incinerated (burned). If they can be used, non-watery liquids will leave the facility in barrels or tank trucks. This is one way of disposing of an emission.

Water will be discharged. Non-hazardous water may be discharged to to a river where it will be diluted and receive additional natural treatment as it flows away, or non-hazardous water may be discharged to a sewer where it will also be diluted and receive additional treatment. Water can be contained. Water must be held in small basins and analyzed to ensure that it is not hazardous. Hazardous water must be returned to the treatment. The consequence of failure of water treatment must be that the water is retained and is re-treated until it is safe for discharge.

Combustible solids will either leave the facility because someone has a use for them (and therefore will be disposed of outside of the facility) or incinerated. Combustible solids cannot be landfilled in Massachusetts. Non-combustible solids must be sealed away from the environment or chemically fixed in some way to make them non-leaching. They can be disposed of on-site, or on a site to which they may be shipped, by storage in a landfill. The landfill must be protected and, monitoring must be carried out both inside and outside the landfill. If hazardous compounds are found to be leaching, the leaching must be stopped by interposition of new seals and barriers or else the landfill must be dug up, treated and moved. The consequence of failure of a landfill, if not correctable, could be the very expensive removal of the landfill.

Combustible sludges normally will be incinerated. Non-combustible sludges normally will be treated, stabilized and disposed of with non-combustible solids.

1.2 Consequences of Failure in Treatment

The consequences of failure for different treatment processes thus differ widely.

Since gaseous emissions cannot be retained the failure of gas cleaning equipment requires shutting down the process. Plans should be drawn to make this as automatic as possible.

Water emissions can be retained so that failure of the treatment poses no immediate hazard. Treatment and analysis must be repeated until the water is pure enough for discharge.

Non-combustible solids (irreducible residues) must be permanently stored. Failures in landfills can sometimes be corrected, but if not, the landfilled material must be dug up and put in a new, safe landfill. Insurance should be available to cover this large expense.

1.3 The Path Followed by Hazardous Waste

Hazardous waste is transported to the facility, analyzed, unloaded, stored and treated to transform hazardous compounds into non-hazardous forms which are safely released or disposed of. The sequence of operations is shown in Figures 1-2 and 1-3, which are different representations of the same idea. Figures 1-2 and 1-3 are intended to help guide the reader through this report. Also, we hope that the Table of Contents will serve as a guide.

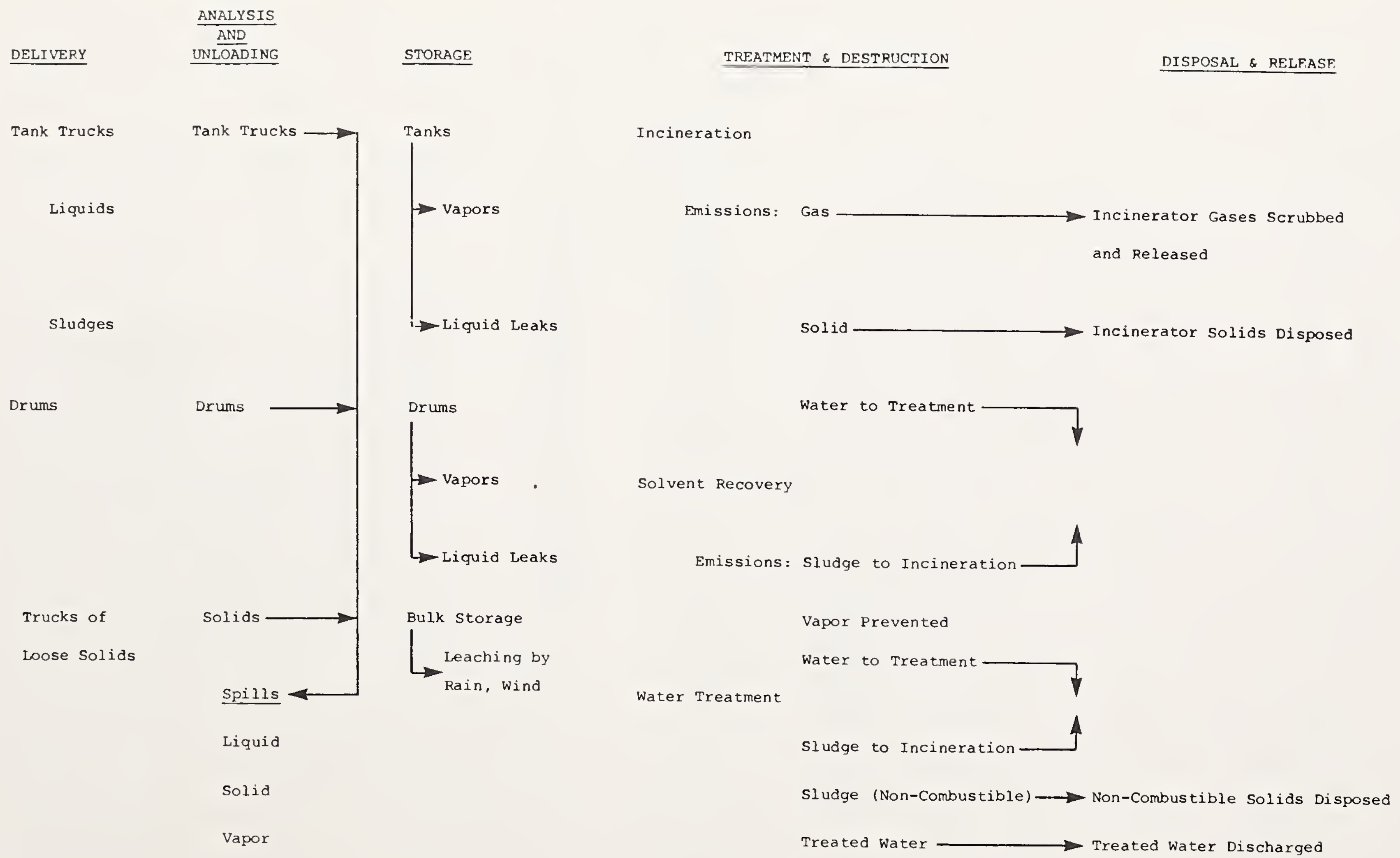

Figure 1-2. Stages in the handling of hazardous waste showing the potential sources of emissions.

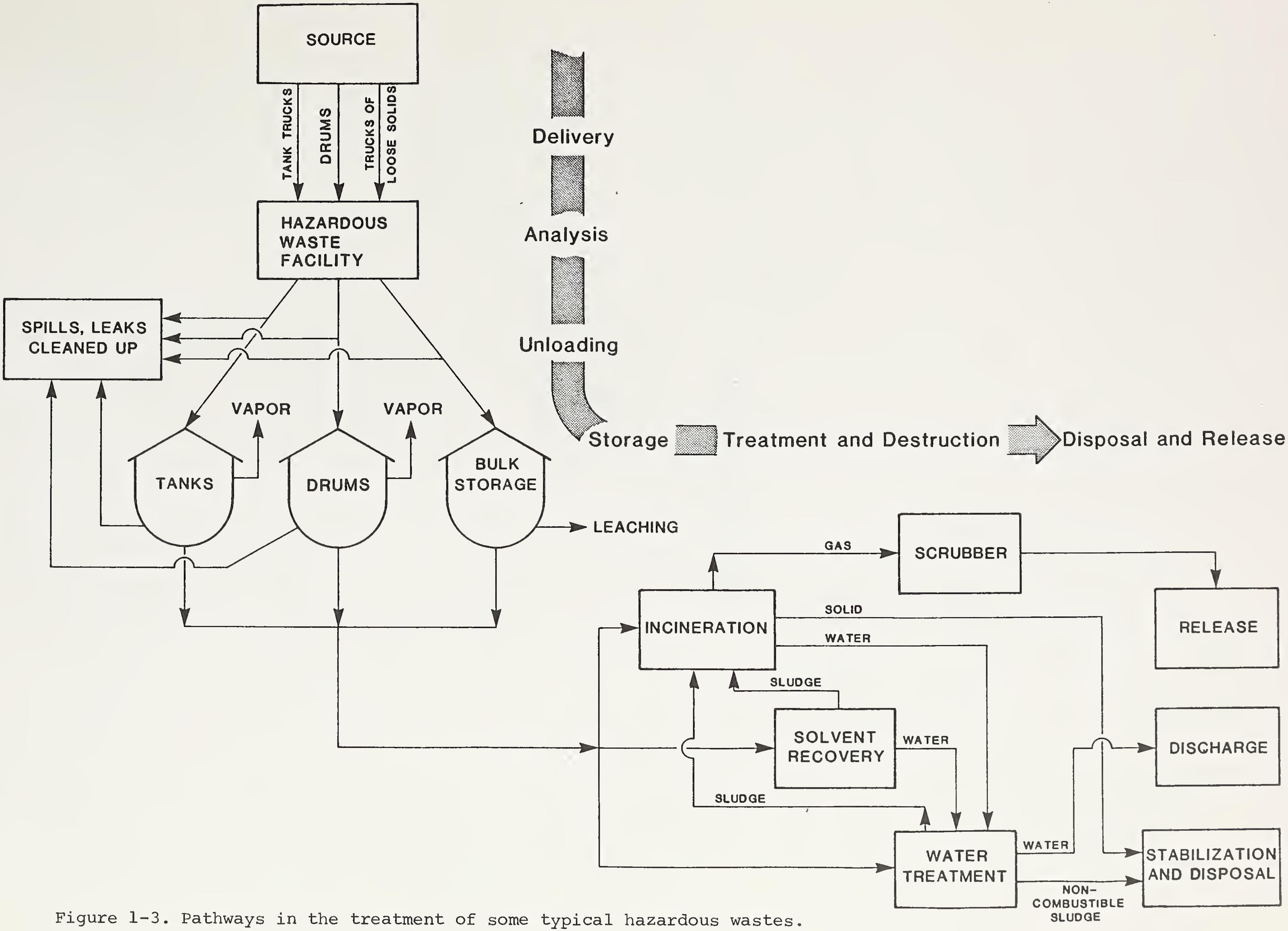

Figure 1-3. Pathways in the treatment of some typical hazardous wastes.

2. DELIVERY OF THE WASTE

2. DELIVERY OF THE WASTE

The wastes will usually be delivered to the facility by road, although a rail line may be possible. An adequate roadway (specifications for which are covered in Massachusetts Department of Public Works regulations), as safe as possible from accidents, will be needed. Consideration should be given to the noise caused by large trucks and the hours during which the road is used.

If an accident does occur during transportation, the facility operator should preferrably be available and prepared to minimize the consequences of the accident. Local fire and police departments may not be equipped to deal with hazardous waste spills and should not be required to do so without the help of the facility operator. The facility operator must have all necessary records and should have made preparation for emergencies in cooperation with local authorities. He also will have available to him assistance from many organizations. The following organizations are among those that have 24-hour telephone answering services which give information on their own products and wastes: Chlorine Institute, Dow Emergency Response Systems (Dow Chemical Company), DuPont Chemical Transportation Emergency Response (DuPont Chemical Company), Shell Chemical Company, National Pesticide Center. Calgon and other firms maintain emergency treatment teams. The Manufacturing Chemists Association maintains CHEMTREC (Chemical Transportation Emergency Center), and most operators and truck drivers are given their 24-hour number. The National Response Center 24-hour line in Washington, D.C. can also be contacted. This Center is run by the Coast Guard on behalf of all the Government agencies. They will contact the duty officer at the EPA Laboratory in Lexington, Massachusetts who has a terminal for the Chemical Information Service computer from which a wealth of helpful data can be promptly extracted.

2.1 Tank Trucks

Most liquids and sludges will be delivered in tank trucks. The construction and use of tank trucks for the transportation of hazardous waste is regulated by the Environmental Protection Agency and the Department of Transportation. Vehicles carrying hazardous waste must be licensed by the Massachusetts Department of Environmental Quality Engineering and the Department of Transportation. The best quality tank trucks for transporting hazardous waste are reinforced circumferentially and longitudinally. There is substantial experience with shipments of hazardous materials in general, which are shipped in quantities 30 to 40 times greater than hazardous waste. Such experience is applicable and should be considered.

2.2 Truckloads of Drums

Drums of solids, sludges and liquids may also be used to ship hazardous wastes. Attention should be paid to type of truck used to carry drums; a closed truck, or high side panel truck, which prevents drums from falling off should be used.

2.3 Truckloads of Solids

Solids may be carried without containers. Attention should be paid to the type of truck used and how the truck is closed to prevent hazardous solids from falling off.

2.4 Transportation Out of the Plant

Materials for reuse, particularly recovered solvents, will be transported out of the plant. Transport out must be as carefully controlled as was transport into the plant.

2.5 Recommendations on Transport

As described in the following sections all incoming waste will be analyzed to decide how to treat it and how to blend it for treatment. Sampling and analysis of waste is difficult and it is most important that the chemist have some idea of what to look for when making the analysis. If one knows what company generated the waste and what that company does one has a good idea of what to analyze for. Waste must arrive at the disposal facility clearly marked as to its source and we recommend that the facility operator have control of the transport. The transportation company must not be allowed to mix in waste of unknown origin. Such mixing is illegal as well as dangerous.

3. ANALYSIS AND UNLOADING

3. ANALYSIS AND UNLOADING

3.1 Analysis

All incoming shipments must be analyzed before unloading. Analysis is necessary before storage because some wastes cannot be safely mixed with other wastes in storage. Analysis is done to determine the appropriate treatment. Details of what is required from the analyses are given in the following sections for each type of treatment.

3.2 Unloading

Unloading requires facilities which have at least the following:

Ability to clean up spilled solids.

Ability to contain spilled liquids, remove the liquid from the containment to storage, clean the containment area.

Ability to trap and destroy vapors and odors.

If containers are washed, facilities must be available to detoxify the wash water.

3.2.1 Unloading and Washing Tank Trucks

Tank trucks will be unloaded by hose directly to storage tanks. This is the best way to unload liquids. Vapor emissions are minimized. If tank trucks are washed, the wash water must be contained and treated.

3.2.2 Unloading, Cleaning and Destroying Drums of Waste

Drums may be unloaded and held without emptying. Full drums are put into the rotary kiln of the incinerator after being punctured or opened just before they enter the kiln. This is the safest way to treat drums of liquid. If liquid is emptied from drums, great care will be required to trap and destroy vapor emissions. If drums are washed, great care will be required to contain the wash water for treatment.

3.2.3 Unloading Loose Solids

The only types of solid hazardous wastes that can be handled in bulk by self-dumping trucks or the like are non-volatile and do not produce quantities of dust. The load in the truck should be covered. Because a few pieces of hazardous solid may remain in the truck after unloading it is best to ensure that the truck is tightly closed for its return journey. If the truck is used on other jobs, a very careful inspection is necessary to ensure that all hazardous solids are taken off.

4. STORAGE

4. STORAGE

4.1 Segregation in Storage

The chemical properties of most wastes are such that they cannot safely be mixed in storage with all other wastes. Analysis must be made to determine whether incoming wastes must be segregated in storage. A responsible person must supervise all unloading to storage at all times. If compatible wastes are to be mixed in a storage tank, the blending of samples of the stored material and the new waste to be added should be carried out on a trial basis in the laboratory.

4.2 Prevention of Spills and Vapors from Storage Tanks

Storage tanks must be set into concrete pits large enough to hold the entire contents of the tanks, in case the tanks leak or burst. The vents on storage tanks must be connected to some system for destroying vapors; this is often the incinerator. Alternatively, tanks may have "conservation vents". These are vents with weighted plugs that do not open under small pressure changes such as those that occur from day to night as the tanks are heated or cooled. However, the vents do open in the event of a high pressure buildup. Venting can prevent an explosion which might otherwise occur with a completely sealed tank.

4.3 Control of Leaks and Vapors from Stored Barrels

Drums of liquids must be neatly stored in an enclosed space which has an adequate floor drain connected to a liquid containment pit, and a vent connected to some system for destroying vapors.

4.4. Safe Storage of Dry Solids

Dry solids must be stored in an enclosed space protected from rain and where hazardous solids cannot be blown around by the wind.

4.5 Fire Prevention and Control

The unloading and storage areas will have to be equipped with automatic sprinklers to stop possible chemical fires, and with an alarm system. Additional mobile firefighting equipment must be available, and only specially trained firefighters should respond to a call. The mobile equipment and trained firefighters might be provided by facility operator or through the local town in its siting agreement.

5. INCINERATION

5. INCINERATION

5.1 Description

Incineration is the name given to the process of burning hazardous waste. The purpose is to convert as much of the waste as possible to water vapor and carbon dioxide. Incineration can be used to destroy solid wastes that contain combustible material, sludges that contain combustible material, combustible liquids that cannot be recovered for reuse, and concentrated solutions of combustible material in water. Incineration is of no use treating non-combustible wastes such as metals and ash, and will probably not be used on dilute solutions in water. If dirty water can be treated by some other method, it should not be incinerated because of the large amounts of fuel required by the incinerator.

One type of incinerator is pictured in Figure 5-1. It contains a "rotary kiln" and a "secondary combustion zone" which together form the "incineration section". It also contains a "gas scrubbing and cleaning section". Both the incineration section and the gas scrubbing and cleaning section are essential to the operation of the incinerator. The two sections will be described separately, but before describing the equipment, it is necessary to understand the purpose of the equipment, that is, the job which it has to do. The purpose of each section can best be introduced by first describing the "emissions" from an incinerator. This follows in Section 5.2. First we give a brief assessment of the reliability of incinerators.

5.1.1 Performance and Reliability

Rotary kiln incinerators of the type shown in Figure 5-1, which are expected to be used in any hazardous waste facility in Massachusetts, have been used for as long as 20 years in Europe and in the United States. Most of them are on the sites of chemical or petroleum processing plants. Very few of them are utilized to destroy hazardous waste from miscellaneous industries; that is, operated as a service to many companies. In Europe there are more incinerators operated as service facilities. A major European installation (started up in 1976) is the Danish national facility (Kummunekemi) in Nyborg. This plant handles all the hazardous waste required to be incinerated in the whole country of Denmark. Another

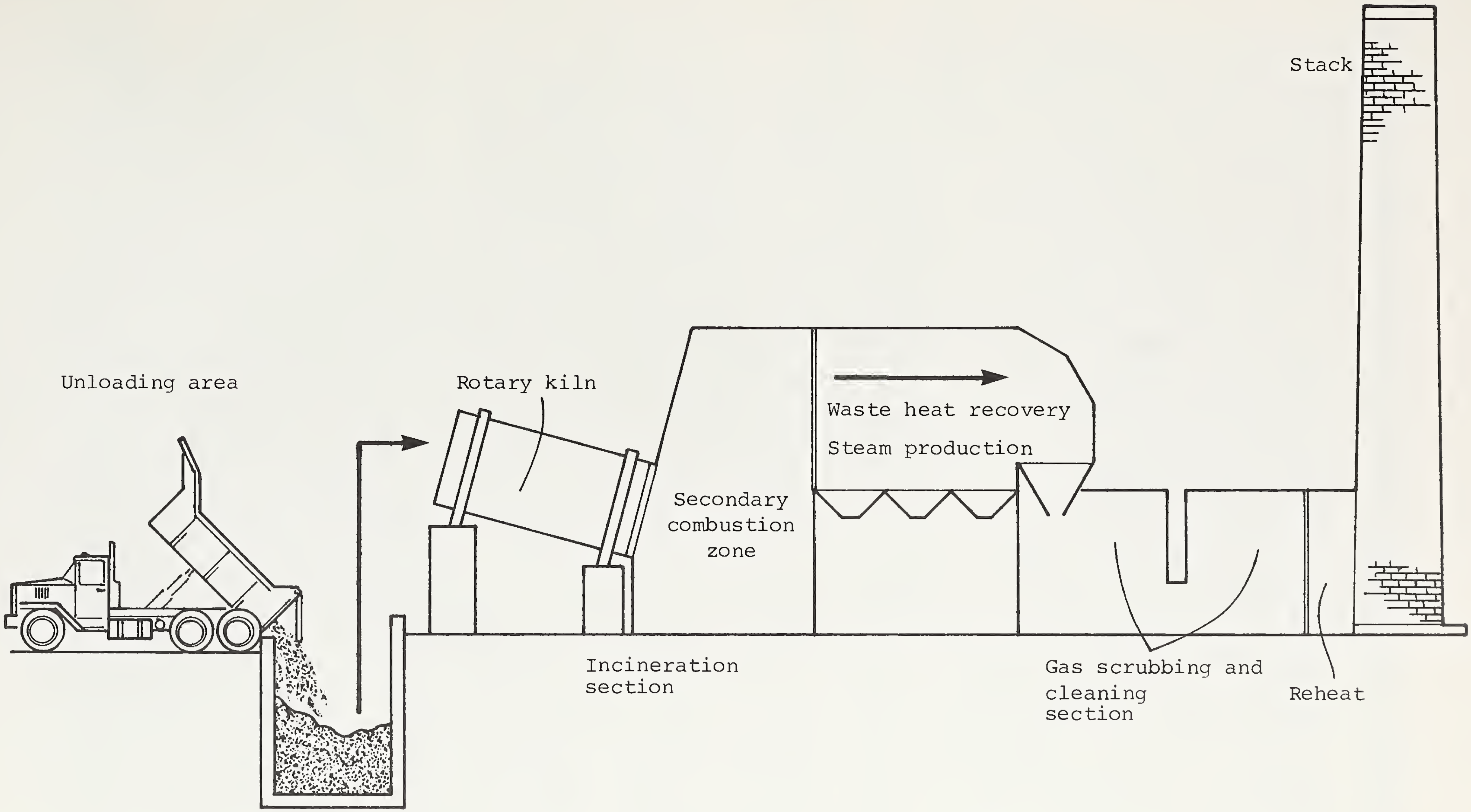

Figure 5-1. Hazardous waste incinerator.

major installation in Ebenhausen handles the hazardous waste of most of Bavaria.

The better quality facilities in both the U.S. and Europe have operated with excellent safety and efficiency records for many years. Unfortunately, the competition between incineration and landfilling of combustible materials in the U.S. has made it difficult for service facility operators to support top quality incinerator designs. The record of some incinerators in terms of operating and maintenance costs has been poor. Nevertheless, the technology is available and there are a number of companies with experience in constructing excellent facilities both here and in Europe.

Landfilling of combustible materials is not permitted in Massachusetts. There are about 340 incineration facilities in the U.S., some for handling solids but the majority only for liquids. The oldest U.S. rotary kiln incinerator facility has been in use since 1960 at the Dow Chemical Company in Midland, Michigan. Other important industrial facilities are at the 3M Company's Chemolite Plant in Cottage Grove, Minnesota, and Eastman Kodak's facility in Rochester, N.Y.

The EPA has conducted performance tests and issued reports on two U.S. facilities that use rotary kilns for solid hazardous waste, the 3M facility and an incinerator belonging to Rollins Environmental Services in Deer Park, Texas (References 2, 3). The 3M plant handles waste only from that company while Rollins performs contract incineration as a service to many industries. The 3M unit is a more sophisticated design but both facilities passed performance tests satisfactorily.

5.2 Emissions from an Incinerator

"Emissions" is the word which refers to the various forms in which the materials put into the incinerator leave, or are emitted from, the incinerator. Remember that matter is not destroyed, it is merely changed in form. For every one pound weight of anything put into an incinerator, one pound weight of something must leave the incinerator. Matter leaves the incinerator mostly as a gas, but also some solid and some liquid leaves. Some combustion calculations on an incinerator are given in Tables 5-8 in a later section. The calculations are for an incinerator rated at "ninety million BTU per hour". In reading the following, it may help to have in mind some of the results of these calculations. The incinerator will burn about 25 barrels of flammable waste (or waste plus fuel) each hour having a weight of about 10,600 lbs. Air, weighing about 13 times more than the waste, is put into the incinerator and 90 percent of this air (all the nitrogen and more than half of the oxygen) comes out of the incinerator and is released up the stack. The volume of stack gas is about 0.5 million cubic feet each hour. This is a cube of gas about 80 ft on each side. The volume of gas is so large that undestroyed waste and other toxic gases are very diluted by the air and are hard to detect and control. Since stack gases are released as they are formed, proper operation of an incinerator requires continuous monitoring.

5.2.1 Gas Emissions from the Incinerator

To understand the dangers of the gas emitted by the incinerator, we must understand what it can contain.

Nitrogen. This is the most plentiful chemical in the incinerator gas. It comes in with air and goes out unchanged. It is non-toxic, colorless and odorless.

Carbon Dioxide. This is the result of burning carbon in the waste and fuel. Carbon dioxide is non-toxic, colorless and odorless; it is formed when any fuel containing carbon is burned.

Water Vapor. This comes from vaporizing water in the waste, from the moisture (humidity) in the combustion air and from burning the hydrogen that was part of the organic molecules in the waste and fuel. It is harmless. Water vapor occurs when any fuel containing hydrogen is burned. Water vapor and carbon dioxide are, next to nitrogen, the gases present in biggest quantities.

Oxygen. Since surplus air is used in the incinerator to ensure complete combustion, there is always some oxygen left over which appears in the incinerator gas. About two and a half times the oxygen needed for combustion is usually added to the incinerator.

The gases described so far (nitrogen, carbon dioxide, water vapor and oxygen) make up about 99 to 99.9 percent of the total gas stream leaving the incinerator section and going to the gas scrubbing and cleaning section. There are other materials in incinerator gas which may be there and which are removed by the gas scrubbing and cleaning section.

Sulfur Dioxide. This comes from burning sulfur that may be in the waste, usually as part of the organic molecules. If the waste contains sulfur, it must be converted to sulfur dioxide to ensure that the waste is destroyed, so sulfur dioxide (and a little sulfur trioxide) should appear in the gas. When sulfur dioxide is wetted, it becomes an acid. Sulfur dioxide appears in the gas when most fuels (oil and coal) are burned. It is the most important source of "acid rain". Most of the sulfur dioxide must be removed from the incinerator gases just as it must be removed from the stack gases of all boilers and furnaces.

Hydrogen Chloride. Hydrogen chloride, with possibly a little chlorine, must appear in the gas when any "chlorinated" waste is being burned. All the chlorine in waste must be converted to hydrogen chloride to ensure complete destruction of the waste. Hydrogen chloride will often appear in the incinerator gas. Like sulfur dioxide, hydrogen chloride and chlorine are "acid". At least 99 percent of the hydrogen chloride must be removed by the gas scrubbing and cleaning section.

Particulate Matter. The phrase "particulate matter" simply means very small particles of solid material. Since the solid will not be carbon (which is completely burned to gaseous carbon dioxide), the older word "soot" is no longer used and "particulate matter" is used. Most wastes, and the fuels used to burn them, contain some material which will not burn. This non-combustible material is ash, mineral matter, pieces of iron from cans, etc., and other metals. An incinerator is designed to keep most of the non-combustibles out of the gas, but some of the smaller particles will always leave in the gas. The scrubbing and cleaning section must reduce particulate matter to a very low concentration.

There are three types of chemicals which should not leave the incinerator section because their removal in the gas scrubbing and cleaning section presents unusual problems.

Hydrocarbons. The waste must be 99.99 percent destroyed in the incinerator.

Carbon Monoxide. This gas is a product of incomplete combustion. It is poisonous. Carbon monoxide will, if there is enough air, burn to carbon dioxide. In a properly run incinerator, carbon monoxide will not occur except in very small quantities.

Oxides of Nitrogen. Nitric oxide (NO) and nitrogen dioxide (NO_2) are always formed when fuel is burned. The mixture is sometimes written NO_x. Oxides of nitrogen are another undesirable product of combustion. The gases are poisonous, form smog and contribute to acid rain. Although much research is going on to determine the best way to remove oxides of nitrogen from stack gas, there is, as yet, no established treatment. The only way to control emissions of oxides of nitrogen is to prevent their formation by controlling the combustion process. Fortunately waste incinerators produce less oxides of nitrogen than do normal boilers or furnaces. There are two reasons for this.

1) Most of the oxides of nitrogen in combustion gas come from nitrogen which is part of the fuel. Waste is, as described later, first roasted in a rotary kiln before it is finally and completely burned in a secondary combustion zone. The roasting breaks down the chemical molecules in the waste and converts nitrogen to molecular nitrogen such as occurs in the atmosphere. This drastically reduces the formation of oxides of nitrogen because molecular nitrogen is oxidized much more slowly than is the form of nitrogen found inside a molecule of fuel.

2) Molecular nitrogen is, slowly and incompletely, oxidized in a furnace. In a normal boiler the amount of air used is not much more than the minimum amount required for combustion. The flame temperature is high and the rate of oxidation of nitrogen is fast enough to produce a range of 200 to 700 ppm nitrogen oxides in the combustion gas. In an incinerator the amount of air used is about two and a half times the amount needed for combustion.

The energy from burning the waste fuel is used to heat up much more gas than in a normal boiler so the flame temperature is lower. This much reduces the rate of oxidation of nitrogen and the expected concentration in the combustion gas is below 100 ppm.

Finally, it must be understood that while an incinerator is excellent for destroying most hazardous wastes, it is not a universally applicable method of destruction. In particular, effort should be made to keep toxic metals out of the incinerator. Many toxic metals vaporize at the temperatures inside an incinerator. The vapor condenses in the cool water of the gas scrubber. Much of the metal is transferred to the water as described on Table 5-1. However, when metallic vapor condenses some solid metal is produced in the form of exceedingly small particles which pass out of the stack with the stack gas. Particles of metal are harmful when breathed. It is extremely difficult to detect small amounts of metals in incoming solid waste. As can be seen from Table 5-1 the first indication that these metals are being fed into the incinerator will come from analysis of the scrubber water, and this analysis should be made periodically.

5.2.2 Solid Emission from the Incinerator

The solid leaving the incinerator is completely non-combustible and has passed through great heat. It is ash and metal. It should be chemically fixed and disposed in a secure landfill. Landfill and fixation are discussed in Section 8.

5.2.3 Liquid Emission from the Incinerator

No liquid can survive the great heat of the incinerator section. All liquid burns or boils and leaves as a gas. The liquid leaving is entirely due to water and chemicals used to scrub and clean the incinerator gas.

Because the incinerator gas usually contains acids which are soluble in water, it is scrubbed with water. The resulting acid may be useful on its own (this is discussed in Section 7.6) or may be neutralized with what are called alkalis. The alkali used may be lime (which is calcium hydroxide), soda ash (which is sodium carbonate) or caustic soda (which is sodium hydroxide). Lime, which is also called slaked lime, is only

TABLE 5-1. METALS THAT VAPORIZE

Mercury; Mercury is a liquid metal which boils. At the temperature of the gas scrubber, the vapor pressure is about 0.2 mm so the stack gas can contain as much as 2.6×10^{-10} ppm mercury or 2×10^{-6} ug/m^3.

Arsenic and Antimony: These metals will partly vaporize as oxides. The vapor is mostly transferred to water in the scrubber, but is difficult to remove from the water.

Cadmium, Selenium, Zinc, Tin and Lead: These metals partly vaporize as oxides and as metal. The vapor is mostly transferred to water in the scrubber and is precipitated by adding alkali to the scrubber water. The precipitate is separated with particulates and fixed.

moderately strong. It can be stored and handled without danger. Soda ash is the same as "washing soda", the major ingredient in household laundry detergents. It, also, can be stored and handled without danger. Caustic soda is lye. It is a good alkali to use for neutralizing, but it must be stored and handled with care. It is a very corrosive chemical when concentrated. Lime is the preferred alkali because of disposal problems caused by sodium.

Neutralization of the scrubbing solution removes acid by chemical reaction to form salts. Thus the neutralized scrubbing solution contains non-poisonous salts in solution. These will be mostly calcium chloride. There will also be some calcium sulfates and sulfites. The calcium part of these salts comes from the alkali and the chloride, sulfite and sulfate comes from the acid gas which was formed by burning the waste.

The neutralized scrubbing solution also contains particulate matter (which in water is usually called suspended solids) and is, therefore, turbid. The used scrubbing solution is recycled many times but finally must be sent to water treatment. Treatment is discussed in Section 7.

5.3 Design Requirements of the Incinerator Section

On Figure 5-2 are shown the various parts of an incinerator in the form of a detailed block diagram. Figure 5-2 is more detailed than Figure 5-1. In the following sections we will discuss each block on this diagram. Delivery and storage have been discussed in Sections 2,3 and 4. The purpose of chemically analyzing the feed to the incinerator is discussed later. In this subsection we discuss the actual incineration - the rotary kiln and the secondary combustion zone. We also describe how combustion must be controlled to ensure destruction of hazardous waste.

Incineration of wastes is called, by chemists, "thermal oxidation". Chemical substances are subjected to a high temperature in the presence of oxygen so that they are oxidized as completely as possible to carbon dioxide and water with lesser amounts of sulfur dioxide, hydrochloric acid and other trace gases resulting from those atoms in the chemicals which were not carbon, hydrogen or oxygen.

Complete oxidation requires a high enough temperature, a long enough time, adequate oxygen and, in the case of solids which do not vaporize, mixing. The rotary kiln ensures mixing. Oxygen is taken from

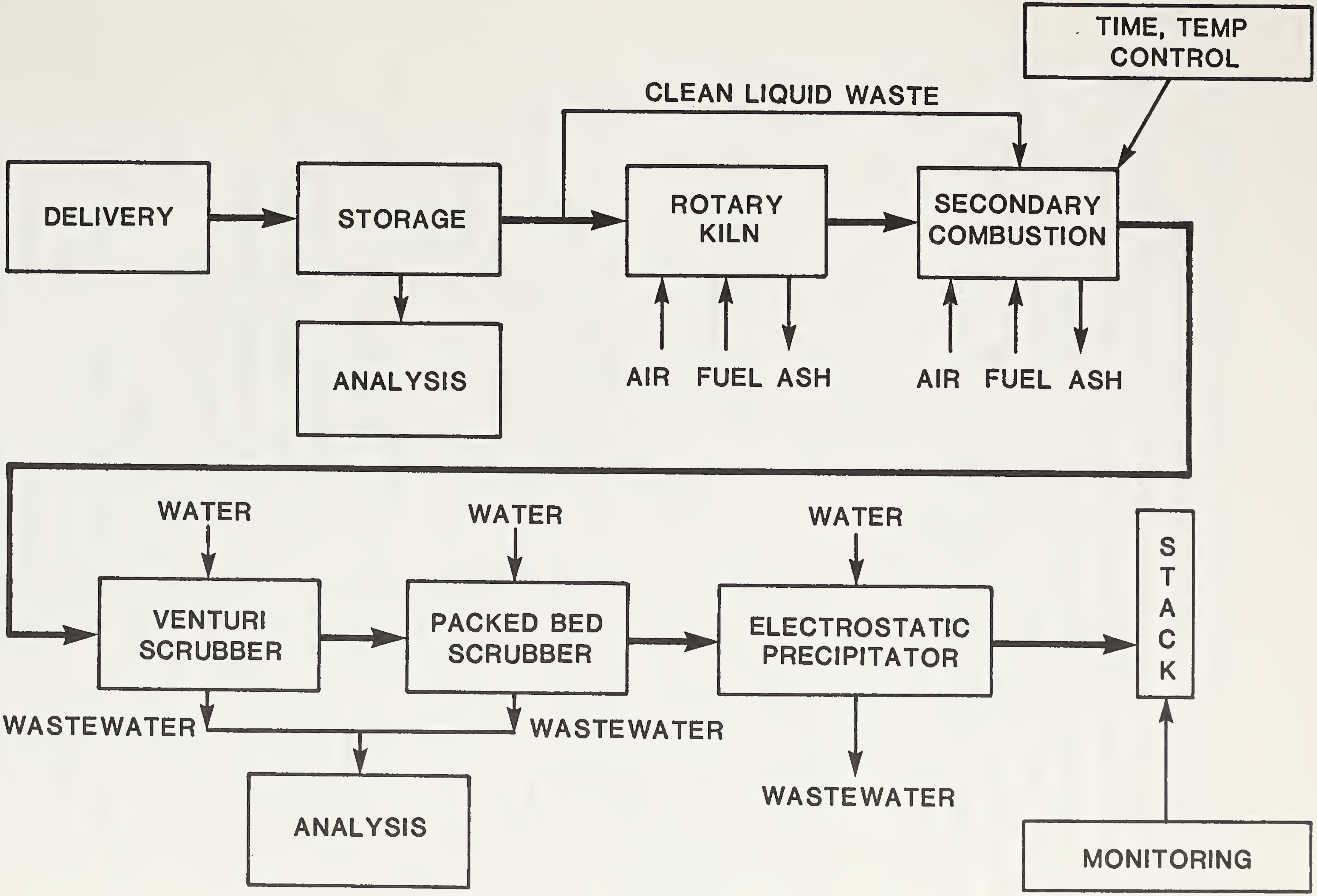

Figure 5-2. Parts of an incinerator.

air and as long as oxygen is found in adequate amounts in the stack gas, one can be sure that enough oxygen for combustion is present.

A high enough temperature is particularly important. Each compound has an "ignition" temperature above which it will oxidize at a reasonable rate. Temperatures higher than the ignition temperature are used so that the rate of oxidation will be fast. Oxidation is not instantaneous and the rate at which a particular chemical oxidizes is faster when the temperature is higher. For example, Hasselriis (Reference 1) reports on the oxidation of toluene. Toluene is a "fuel" because it gives off enough heat on oxidation to support continuing oxidation. (Oxidation is the same as combustion or burning). At 1410°F (= 766°C) toluene is 99.99 percent oxidized in 0.3 secs. At 1530°F (= 832°C) toluene is 99.99 percent oxidized in 0.1 secs.

However, the waste incinerator will have to destroy mixtures, not pure compounds like toluene. Mixtures contain compounds that are more difficult to destroy than toluene and will require a longer time at a higher temperature than toluene.

The Environmental Protection Agency has sponsored tests on burning difficult wastes that consist of mixed hazardous compounds with water (References 2 and 3). The equipment pictured in Figure 5-1 was used, and it was found that adequate oxidation (which by law means 99.99 percent destruction of the waste) occurred, for most compounds, at temperatures in the range 1800° to 2000°F for 2 secs. Chemicals that are particularly resistant to oxidation, which are mostly chemicals that do not themselves burn, require up to 3 secs at 2400°F for destruction.

Note that although time and temperature are used by the facility operator to control the destruction of the waste, the regulatory requirement placed on the operator should be 99.99 percent destruction as monitored by analysis of the stack gas as described later.

Figures 5-1 and 5-2 show two parts to the incineration section, a rotary kiln and a secondary combustion zone. The most important reason for the rotary kiln is to partially oxidize and vaporize solid waste and to give liquids that are inside drums plenty of time to vaporize. A solid or liquid spends a long time, measured in minutes not seconds, in the rotary kiln. Once a chemical is vaporized, it is swept along in the air and combustion gases and spends seconds, not minutes, in the kiln.

The kiln and the secondary combustion zone have separate burners in which fuel is burned to provide heat. The fuel will usually be a liquid, unless natural gas is used, and will be atomized into the air to burn with a strong flame. The fuel may be purchased fuel or liquid waste which has a high fuel value. On Figure 5-2 we show clean liquid waste bypassing the rotary kiln and being atomized directly into the secondary combustion zone. In the secondary combustion zone vapors are burned. The residence time necessary for adequate destruction of the waste must be provided for vapors in the secondary combustion zone.

5.3.1 Control of Incineration

Control of time and temperature in the secondary combustion chamber is essential for adequate incineration. The time is controlled by controlling the feed rate of air to all parts of the incinerator. Since 80 percent or more of the gas sweeping through the secondary combustion chamber is air, control of the air rate will control the length of time required for the gas to pass through the secondary combustion chamber.

To keep the temperature high enough, fuel must be added as needed, particularly if the waste burns with difficulty or does not support its own combustion. On the other hand, waste that is particularly easily burned must not be added too fast or the temperature will go too high. Too high a temperature encourages the formation of oxides of nitrogen and must be avoided.

5.4 Design Requirements of the Scrubbing and Cleaning Section

The gas cleaning equipment has to selectively remove the small quantity of pollutants present in the incinerator gas stream, while allowing the bulk of the gas to pass through the system unchanged. To do this, the cleaning equipment must make use of some physical or chemical property of the pollutant that is markedly different from that of the bulk gas stream. The properties of solids, or particulate matter, that may be used to separate them from the gas stream are their discrete size, greater density and electrical conductivity. Removal of specific gases generally relies on their greater solubility in water than the bulk gas. Figure 5-3 shows some of the methods that may be used for control of solid and gaseous pollutants. Wet scrubbing is briefly

TYPE OF EMISSION	
Particulate	Gas and Vapors
Wet Scrubbing	Wet Scrubbing
Electrostatic Precipitation	Adsorption
Cyclonic Separation	Catalytic Combustion
Fabric Filtration	Thermal Incineration

Figure 5-3. Particulate and gaseous pollutants control equipment.

described below, followed by a description of the preferred equipment.

Wet Scrubbers

Wet scrubbing is the one method shown in Figure 5-3 that is applicable to both particulates and gases. It is the best method for removal of acid gases. The gas stream is brought into intimate contact with water which dissolves the soluble gases. Water is the preferred scrubbing liquid as it is cheap and is itself not a pollutant. The gases in the incinerator waste gas are summarized in Table 5-2 together with their solubility in water and alkaline solution. As can be seen, the non-toxic gases nitrogen, oxygen and carbon dioxide are only slightly soluble in water. Hydrogen chloride, hydrogen fluoride and sulfur trioxide are very soluble, and chlorine and sulfur dioxide are moderately soluble.

A water scrub will remove the gases that are moderately or very soluble. The most important are hydrogen chloride and sulfur dioxide. The toxic gases that are not readily soluble in water are nitrogen oxides, carbon monoxide and hydrocarbons. These gases are not removed by the scrubbing system and their formation in the incinerator must be minimized by maximizing destruction of waste by using a long enough time and the correct temperature (neither too low nor too high).

When the soluble gases dissolve in the water, the water becomes acidic and must be neutralized by the addition of alkali before it can be disposed of. It is usual to add the alkali to the recirculating scrubber water since this effectively increases the solubility of all the acid gases. The salts formed on reaction of the acid gases with the alkali are generally nontoxic, but must be removed from the circulating scrubbing water to prevent their becoming too concentrated and precipitating out. A small bleed or "blowdown" stream is therefore continuously withdrawn to the water treatment system, while alkali is added to the circulating water. Figure 5-4 shows a typical flow scheme. The water treatment is discussed in Section 7.

Wet scrubbers also remove particles from the gas by wetting them and then either trapping them in the liquid or separating them from the gas by utilizing the greater size and density of the wetted particles. The

TABLE 5-2. IMPORTANT GASES AND THEIR SOLUBILITY IN WATER AND ALKALI

Gas and Chemical Formula or Abbreviation		Solubility in Water	Solubility in Alkali
Nitrogen	N_2	Slightly	Slightly
Oxygen	O_2	Slightly	Slightly
Carbon dioxide	CO_2	Slightly	Very
Hydrogen chloride	HCl	Very	Very
Hydrogen fluoride	HF	Very	Very
Sulfur trioxide	SO_3	Very	Very
Chlorine	Cl_2	Moderately	Very
Sulfur dioxide	SO_2	Moderately	Very
Nitrogen oxides	NO_x	Slightly	Slightly
Carbon monoxide	CO	Slightly	Slightly
Hydrocarbons	HC	Slightly	Slightly
(Particulates)	-	Not generally	Not generally

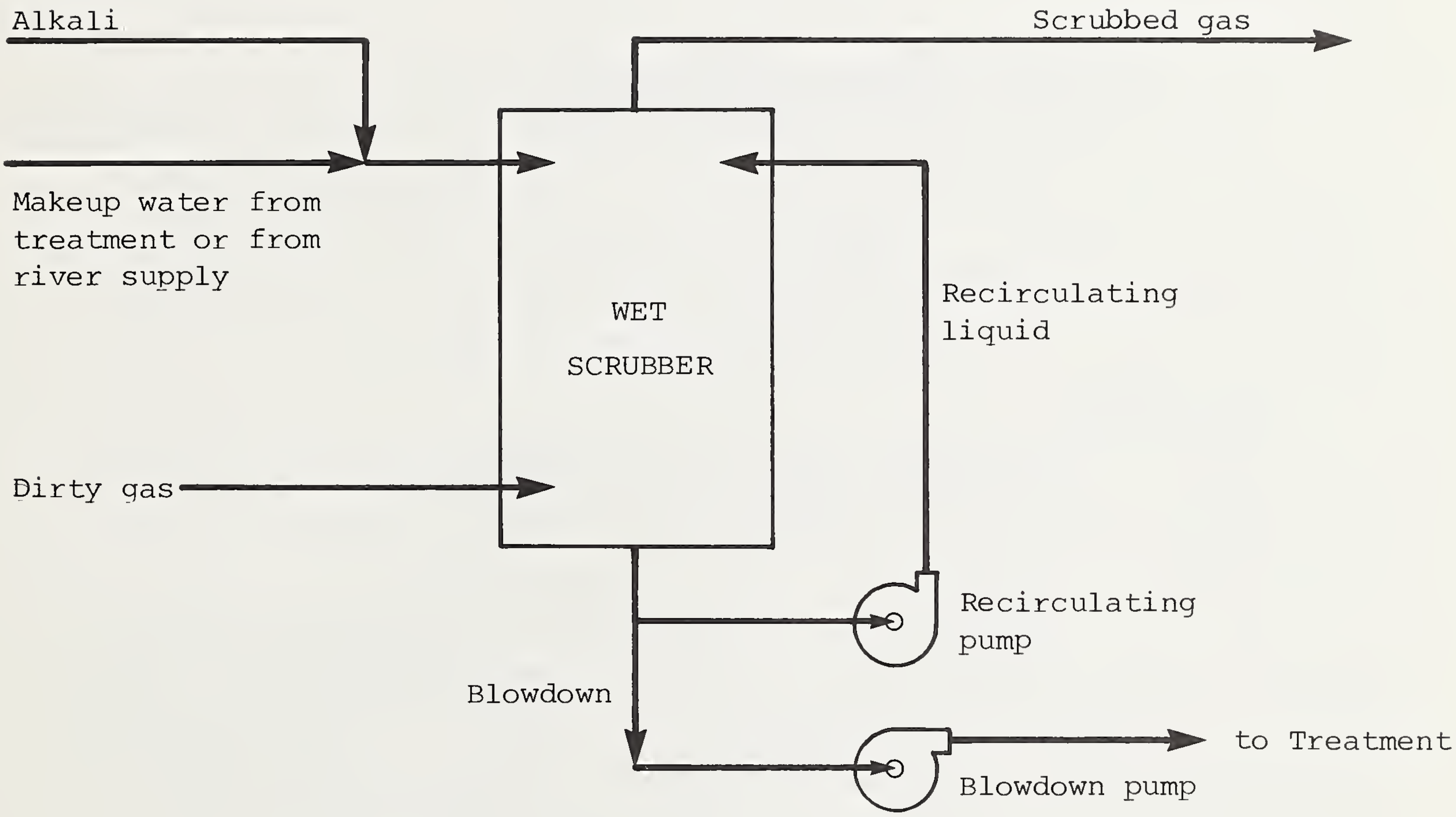

Figure 5-4. Typical flow scheme for a wet scrubber.

greater the particle size, the easier it is to remove the particle. Particle sizes are measured in micrometers (microns); a micrometer is one-millionth of a meter, (one-thousandth of a millimeter) or 1 μm. A typical bacterium is about 2 μm in size. Particles from an incinerator burning a liquid waste may be smaller than this, while sizes may average anywhere from 5 to 100 μm when burning solid wastes. It is clear that we are dealing with very small, difficult to remove particles, and the wet scrubbing equipment must be selected accordingly. The equipment is described next.

5.4.1 Preferred Scrubbing and Cleaning Equipment

The gas cleaning devices that will probably be used with an incinerator are a wet Venturi scrubber followed by a wet packed scrubber, plate scrubber, or cyclone. To complete the removal of particulates, an electrostatic precipitator designed for wet service will be the third device in line. This is the sequence shown on Figure 5-2.

Wet Scrubbers

Because both particulate and gaseous pollutants require control, a wet scrubber will normally be the preferred, but not necessarily the only, method of treatment.

Particulate removal in a wet scrubber is accomplished by wetting the particles to increase their size and by trapping them in the liquid. Gases are removed by being dissolved in the liquid. In both cases it is necessary to bring the gas and the liquid into close contact. The simplest method is to pass the gas through a liquid spray as shown in Figure 5.5. A spray column has the advantage of having a low pressure drop, that is, the energy necessary to pass the gas through the column is small. However, removal efficiencies are likewise low, and a spray column is useful only for partial removal of very soluble gases or for removal of large-sized particles, say greater than 10 to 20 μm. As we have seen, particle sizes in an incinerator gas stream may be down to 1 to 2 μm or less, and therefore spray towers will not usually be used. There are several types of wet scrubbing equipment that can achieve greater efficiencies than the simple spray column, but the one most appropriate to incinerator gases is the Venturi scrubber.

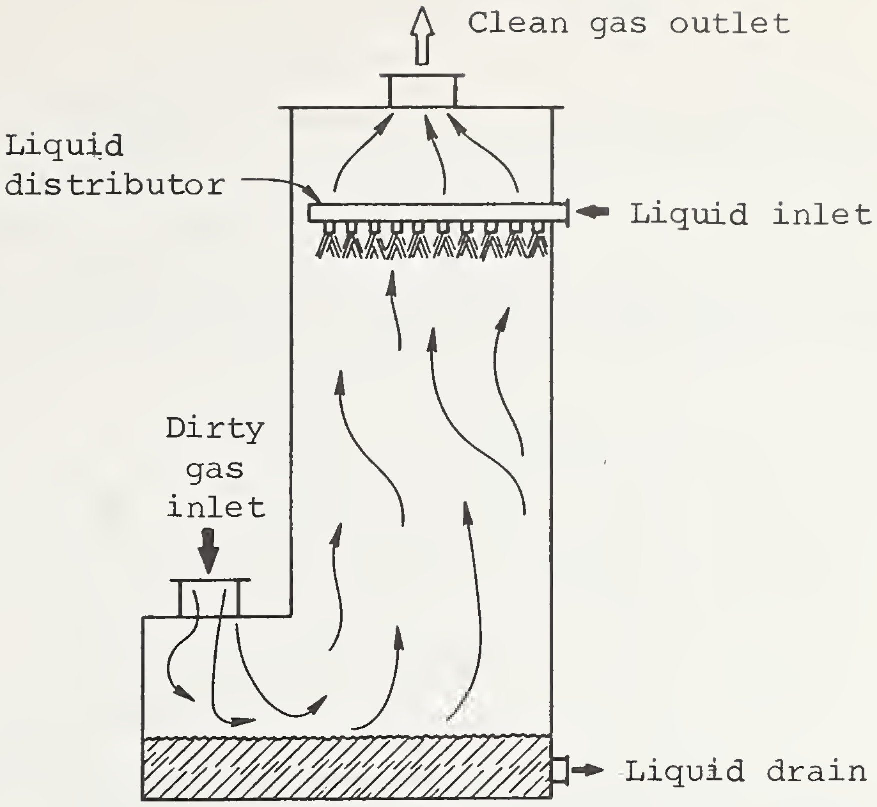

Figure 5-5. Open spray tower.

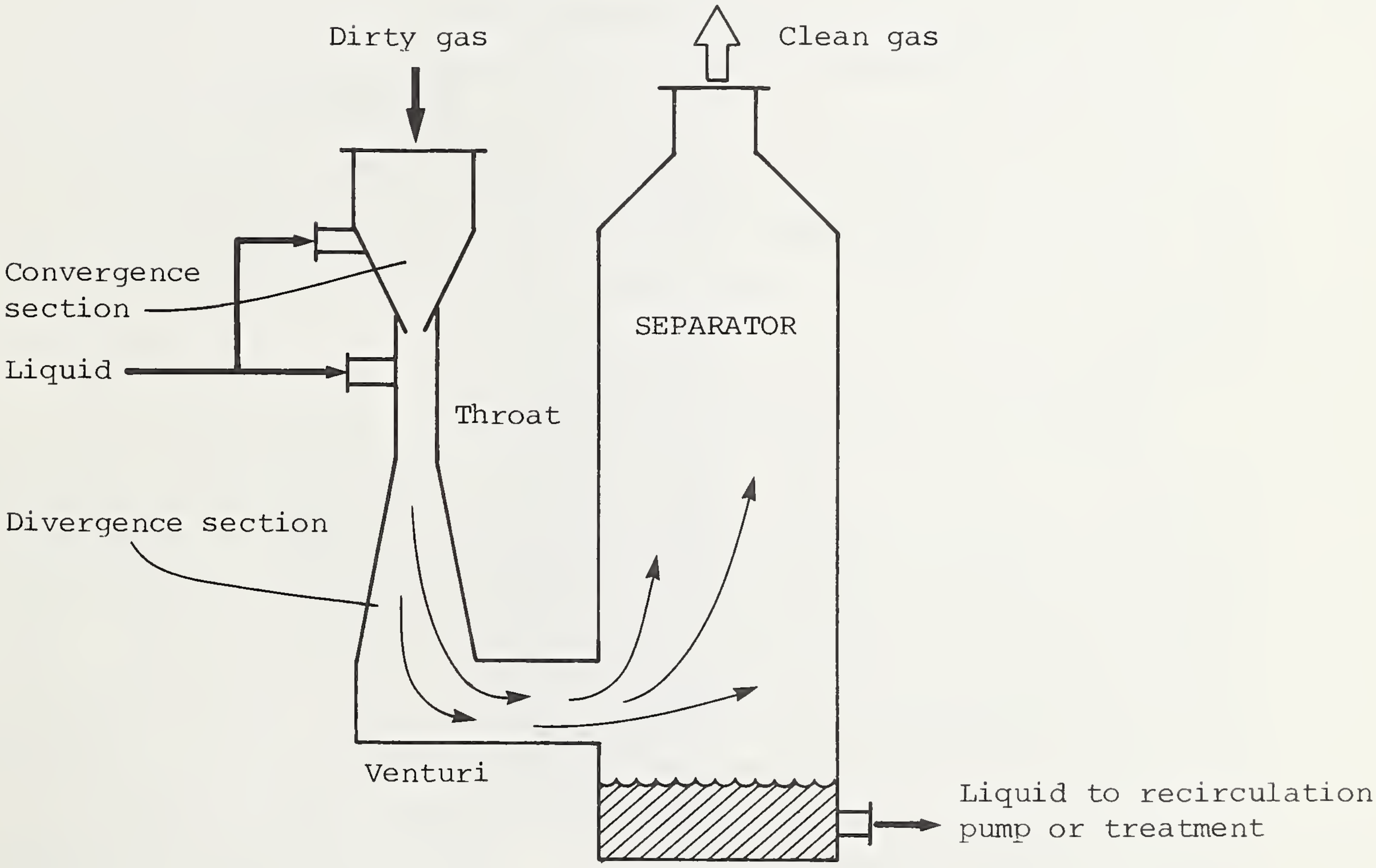

Figure 5-6. Variable throat Venturi scrubber.

The Venturi scrubber illustrated in Figure 5-6 is capable of high particle collection efficiencies, and is effective for particle sizes down to 1 μm and less. The Venturi scrubber consists of two sections. The Venturi section is essentially a contracting/expanding pipe in which the gas is accelerated to high velocities. At these high velocities, the liquid which is sprayed in just upstream of, or at, the narrowest section (called throat) of the Venturi, is broken up into a very fine mist. This promotes good contact between particles and liquid and insures that the particles are wetted. The heavier, wetted, particles are then removed in a disentrainment section which is typically a cyclone, plate or packed separator (discussed later). High gas pressure drops occur in the Venturi; the higher this pressure drop the greater the particle removal efficiency. Removal efficiencies can also be improved by circulating greater quantities of liquid. These effects are shown in Figure 5-7.

Although the Venturi scrubber is effective for removing soluble gases, its best function is removal of particulates. Better removal of gases can be obtained in other contacting devices. One such device is the scrubber illustrated in Figure 5-8. A Venturi scrubber followed by a packed scrubber can be used to achieve good control of both particles and gases. The packing is designed to give repeated contact between the gas and the scrubbing water. The inclusion of a mist eliminator, typically a fine wire or plastic mesh, at the exit of the column will control acid mist.

Electrostatic Precipitators (ESP)

The ESP is a device for removing particulate matter from gas streams. It does not remove gases, but can remove particles in the same range as a medium to high pressure-drop Venturi scrubber. Unlike the Venturi scrubber, the ESP has a very low pressure drop, although its overall costs may be similar to or higher than a Venturi system. The ESP collects particles by imposing a charge on them, and collecting the charged particles on an oppositely charged collection plate. The collecting plates are irrigated with water to which a small amount of alkali is added to make it conductive. This water stream neutralizes the charged

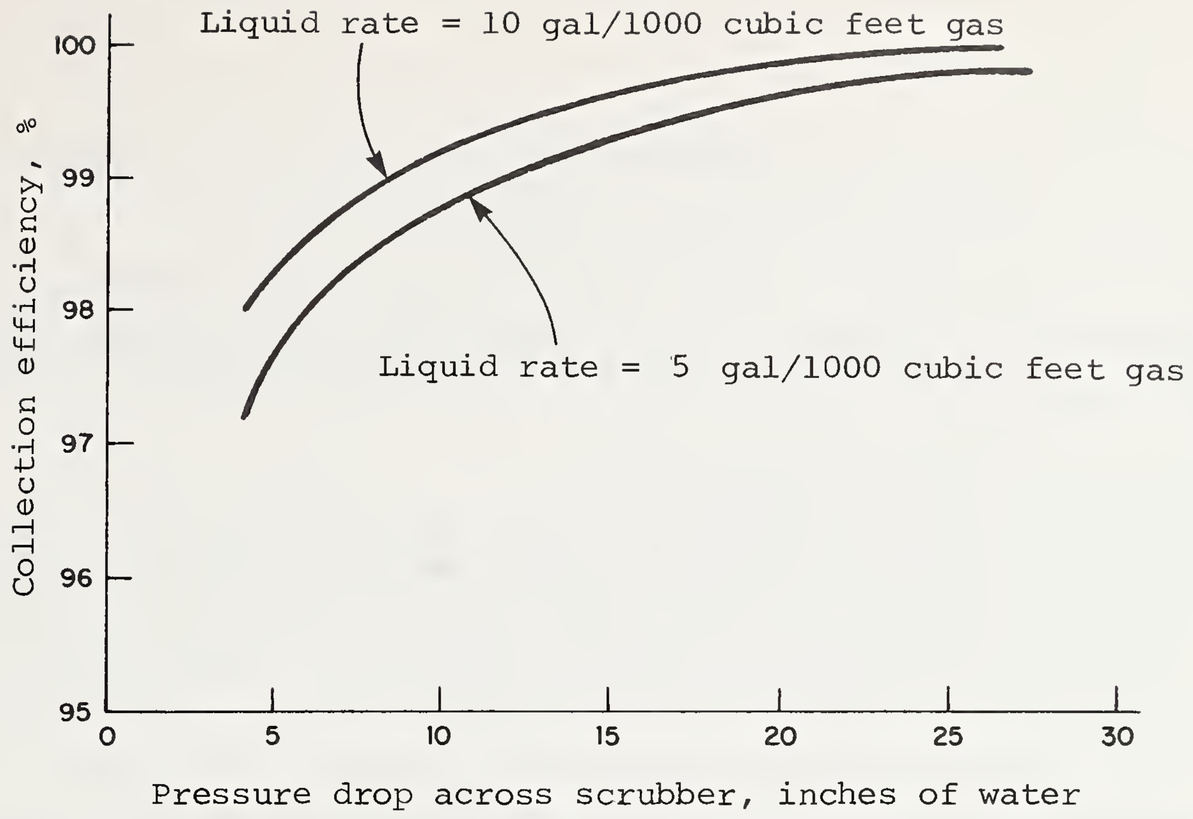

Figure 5-7. Effect of pressure drop and liquid rate on collection efficiency of particulates for a Venturi scrubber.

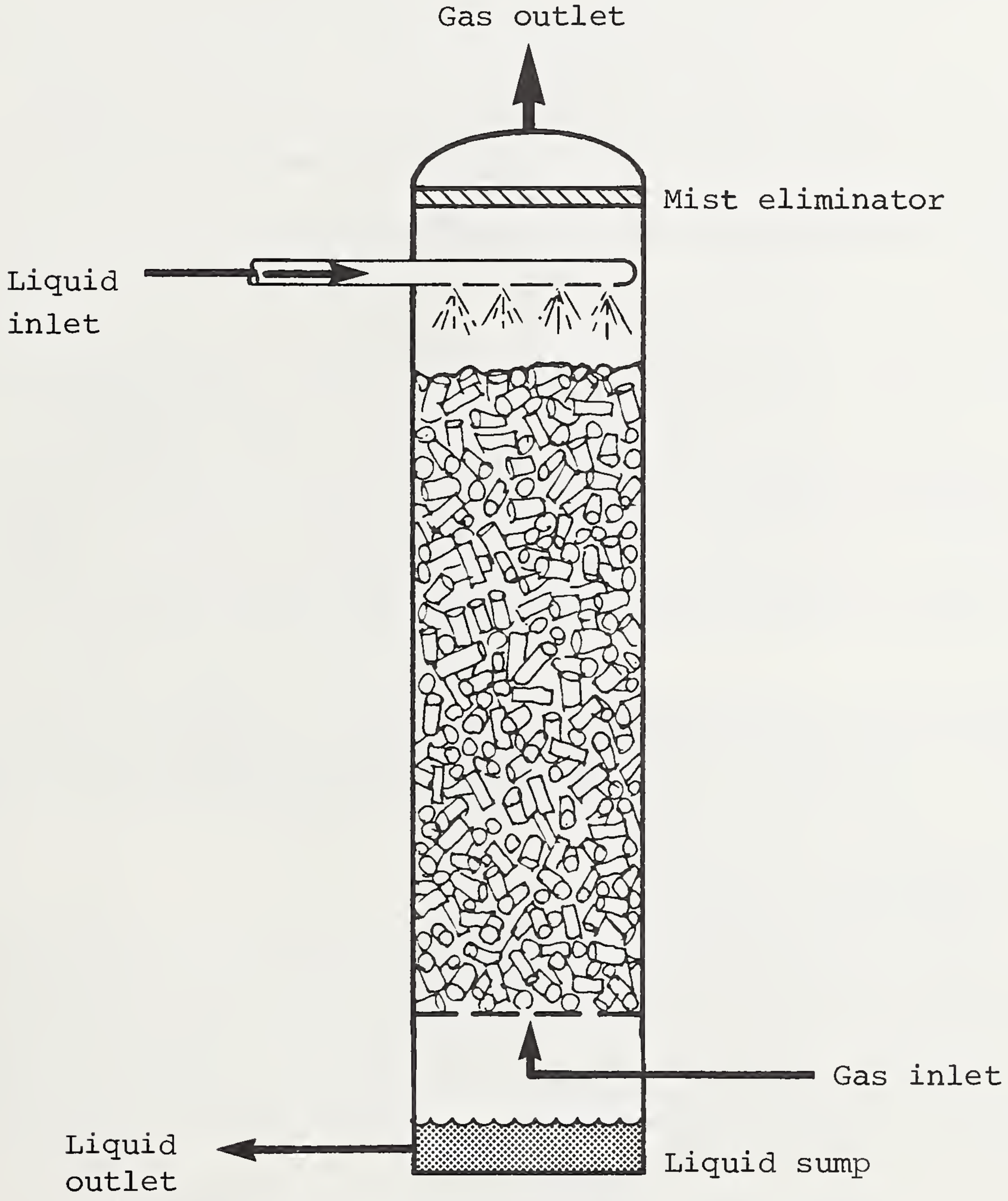

Figure 5-8. Schematics of packed scrubber.

particles as they reach the collector electrode and carries them off in the same way as in the wet scrubber system.

ESP's have been used for many years with excellent results, particularly in the electric power industry. It is nevertheless imperative that they be operated correctly.

5.5 Quality of Incinerator Stack Gas

Since some pollutants (carbon monoxide, hydrocarbons and nitrogen oxides) are not removed in the scrubbing and cleaning section, and since the scrubbing and cleaning section cannot remove 100 percent of the other pollutants (sulfur dioxide, hydrogen chloride and particulates), some pollutants will be emitted from an incinerator. In this section we show how much pollutant will probably be emitted and what this means. This is done in three subsections. First, we discuss the reasonable concentrations of pollutants in the atmosphere as defined by the legal air quality standards and by actual measurements of air quality. In this regard, two points should be kept in mind. The first is that pollutants do not remain forever and accumulate in the atmosphere. Most of the gases are washed out by rain (sulfur dioxide, hydrogen chloride, nitrogen dioxide, hydrocarbons). Measurements also show that carbon monoxide does not accumulate, although the way in which it disappears from the atmosphere is not understood (Reference 9). The second point is that much or most of the polluting gases in the atmosphere come from nature or from non-industrial sources of great social importance, such as the automobile. A hazardous waste facility adds to the pollutant load in the atmosphere. The question we ask is - how much does it add?

In the second subsection the probable rates of production of pollutants are estimated.

Finally, in the third subsection the rates of production of pollutants are converted to concentration units in the atmosphere and the effect on ambient air quality is discussed.

5.5.1 Ambient Air Quality

First, there are regulations on what may legally be emitted from a waste incinerator. Table 5-3 shows the provisional EPA regulations currently in force. Not all of this information is helpful in understanding how an incinerator affects the atmosphere. However, the requirement

TABLE 5-3 HAZARDOUS WASTE INCINERATION FACILITY AIR EMISSION STANDARD

The interim-final hazardous waste incineration emission standards were issued in the Federal Register Vol. 46, No. 15, Friday, January 23, 1981, pp. 7666 to 7690. The standards may be summarized as follows:

1. Total organics removal of 99.99% of feed is required. This will be determined by monitoring several of the least combustible constituents to be sure that 99.99% of those materials are destroyed.
2. If the feed contains more than 0.5% organically bound chlorine, 99% of HCl must be removed by scrubbers.
3. Particulate emissions may not exceed 0.08 grains per dry standard cubic foot (180 mg per dry standard cubic meter).

In addition, the following proposals are presented in the interim final regulations:

1. The requirement of 99.99% organics removal may be raised or lowered depending on ambient conditions.
2. Metals and other inorganics may also be limited, based on risk assessment on a site-specific basis.
3. Products of incomplete combustion may not exceed 0.01% of original organic compounds.

There is no estimate of when final regulations will be promulgated or whether the three proposals will be included.

that 99.99 percent of waste must be destroyed is relevant. In Section 5.5.2 we use, as an example, a single large incinerator which is probably what will be installed in Massachusetts. This incinerator burns a maximum of 10,000 lbs. of waste each hour which is 50 percent water and 50 percent dry waste. The maximum permitted emission of waste is, therefore, one half a pound per hour or less than 2.5 tons/year.

Federal Ambient Air Quality Standards are a measure of what it is safe to breath. The longer one breathes contaminated air the lower the concentration of pollutant must be if the air is not to be unhealthy. Examples are shown on Table 5-4. Of most interest is the quality of the air which can safely be breathed continuously. The annual averaged standards (continuous exposure) are shown in Table 5-5.

Of equal or greater interest are actual measurements of air quality. These measurements vary a great deal. The following information is taken from Reference 9 and 10.

Carbon Monoxide. Measurements of the concentration of carbon monoxide are particularly varied, even in non-urban areas. Carbon monoxide has a life of from one-third to three years in the atmosphere and, therefore, is carried by the wind long distances from the source of its generation. This may account for the variations found. The range measured is about 60 to 1,200 $\mu g/m^3$. Eighty-six percent of the emissions of carbon monoxide are from automobiles and trucks.

Nitrogen Oxides. In most cities, nitrogen oxides in the atmosphere in daytime are in the range of 40-80 $\mu g/m^3$. Since at least half of the nitrogen oxides come from automobiles, this concentration range will be found in rural areas if near a large road. Far away from traffic, the concentrations will be lower. The second major source of nitrogen oxides is central electric generating stations.

Hydrocarbons. Non-urban air contains about 700 - 1,000 $\mu g/m^3$ of the gas methane. This gas, also called marsh gas, results from bacterial decay such as in a compost or manure heap. Other hydrocarbons are present at below one-tenth the concentrations of methane. Ninety-six percent of the emissions of other hydrocarbons are from automobiles and trucks.

TABLE 5-4 FEDERAL AMBIENT AIR QUALITY STANDARDS

Units: Micrograms/cubic meter ($\mu g/m^3$)

Pollutant	Averaging Time	Primary Standard
Sulfur oxides	Annual	80
	24 h	365
Particulates	Annual	75
	24 h	260
Carbon monoxide	8 h	10,000
	1 h	40,000
Hydrocarbons	3 h	160

TABLE 5-5 ANNUAL FEDERAL AIR QUALITY STANDARDS

Pollutant	Concentration ($\mu g/m^3$)
Sulfur oxides	80
Nitrogen oxides	100
Particulates	75

Sulfur dioxide. In Chicago, measurements have ranged between 340 and 85 μg/m^3. The value of 340 μg/m^3 was found to be highly corrosive to steel test panels. In New York, a similarly high concentration of 285 μg/m^3 at 50 percent relative humidity reduced visibility to 5 miles. In non-urban areas a typical concentration is about 25 μg/m^3. The major source of sulfur dioxide is central electric generating stations.

Particulates. Particulate concentrations vary drastically over a few hours as wind rises and falls and lifts dust from the ground. Annual average concentrations range from 60 to 200 μg/m^3 in urban areas and 10 to 60 μg/m^3 in non-urban areas. About 80 percent of the emissions of particulates are from central electric generating stations.

With this background information on ambient air quality we go on to estimate the emissions from an incinerator. The emissions can then be compared to the background ambient air quality. Before going on, a brief digression is necessary to discuss the units in which concentration is reported. So far we have used micrograms per cubic meter which is a weight of pollutant per volume of air. For gases, but not for particulates, concentrations are sometimes reported in volume of pollutant per volume of air, or parts per million by volume (ppm (Vol.)). The conversion depends on the gas, and the multipliers are tabulated in Table 5-6.

TABLE 5-6 CONVERSION OF CONCENTRATION UNITS

To convert microgram/cubic meter (μg/m^3) to parts per million by volume (ppm (Vol.)), multiply by

Carbon Monoxide (CO)	0.00080
Nitric Oxide (NO)	0.00075
Nitrogen Dioxide (NO_2)	0.00049
Methane (CH_4)	0.0014
Sulfur Dioxide (SO_2)	0.00035
Hydrogen Chloride (HCl)	0.00061

5.5.2. Quantity and Composition of Incinerator Stack Gas

To determine the quantity of incinerator stack gas, the size of the incinerator must be known. Size is measured in heat output, and a size of 90 million British thermal units (Btu) per hour is assumed. This is the size expected to be installed in Massachusetts. A pound of fuel oil yields about 17,500 Btu when burned. Wastes, however, do not have as high a heating value as fuel oil, mostly because they are wet. Some heating values that have been found in practice are listed on Table 5-7. Waste oil is an excellent fuel, nearly as good as regular fuel oil, but most other wastes have from one third to one half the heating value of fuel oil. For estimating purposes we have assumed a heating value of 8,500 Btu/lb. The incinerator will, therefore, handle an average of 90 million/8,500 = 10,600 lb. waste per hour (this is equivalent to about 25 drums of liquid waste per hour).

With this information, the major components of the stack can be estimated. For readers conversant with chemical calculations, the calculation is given on Table 5-8. However, the calculations have to be made in molar units, which are units of chemical equivalence. We apologize that Table 5-8 is not useful for the reader who is not a chemist. The results are that the major components of the stack gas will be about:

	lbs/hr	Volume Percent
Nitrogen	108,000	73.0%
Oxygen	17,000	10.3%
Carbon Dioxide	17,000	7.3%
Water Vapor	9,000	9.2%
Hydrogen chloride	300	0.2%

Please remember that this is only an estimate. The actual composition of the gas depends on the composition of the waste and on the water content of the waste. The composition of the stack gas will vary. However, variations of more than 25 percent are improbable.

We now need to know the quantities of pollutant gases released. Based on a probable mixture of waste that will be burned in an incinerator in Massachusetts, IT Corporation (Reference 8) have estimated the release of these gases in tons per year. On Table 5-9 are shown the IT numbers

TABLE 5-7 AVERAGE HEATING VALUE OF WASTE SENT TO INCINERATION

Information from Kommunekemi, Denmark:

	Btu/lb
Waste Oil	17,100
Pumpable Solvent Waste	6,300
Pumpable Organic Chemical Waste	6,300
Viscous Organic Sludge	6,300
Solid Waste in Packages (mostly paint residue)	6,300
Solid, Unpackaged waste with Organic Contamination	900*

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*Requires added fuel.

Information from IT-Enviroscience:

Average 8,000 to 9,000 Btu/lb

The most important non-combustible is water.

Chlorinated organics average 5 to 10%, from which we estimate that chlorine averages 3%.

TABLE 5-8 ESTIMATION OF INCINERATOR STACK GAS QUANTITY AND COMPOSITION

Incinerator size: 90×10^6 Btu/hr

Range of heating values of fuel and waste burned: 17,000 Btu/lb for waste oil to 6,000 Btu/lb for wet waste. (Wastes having a heating value below, about, 6,000 Btu/lb will be mixed with fuel to maintain adequate incineration temperature).

Average heating value for exemplary calculation: 8,500 Btu/lb

Assumed composition of the waste:

Combustibles taken to be -CH-. (-CH- has been chosen, rather than $-CH_2-$, to allow for oxygen in the waste chemicals.) Since -CH- has a heating value of 18,000 Btu/lb the waste is assumed to be

47%	-CH-
3%	Chlorine
50%	Water

which has a heating value of 8,500 Btu/lb. The percent chlorine is based on experience in the chemical industry.

Rate of incineration of average waste: $90 \times 10^6/8,500 = 10,600$ lb/hr

Yield of combustion products:

Carbon dioxide - $10,600 \times 0.47/13 = 383$ lb moles/hr

Water (from combustion) = 192 lb moles/hr

Minimum oxygen required: 479 lb moles/hr

Nitrogen from air to give minimum oxygen: 74/21 (oxygen) = 1,800 lb/moles/hr

Let X be the pound moles per hour of excess air added to control combustion temperature at 2,000°F.

Stack gas composition:

	lb moles/hr	10^3 Btu per lb mole @ 2,000°F	10^6 Btu/hr @ 2,000°F	lb moles/hr with X = 2,600
Carbon dioxide	383	23.0	8.9	383
Water	486	37.0	18.0	486
Hydrogen chloride	9	14.0	0.1	9
Oxygen	0.21X	15.4	0.0032X	546
Nitrogen	1800 + 0.79X	14.5	26.1 + 0.011X	3,854

Total heat = 90×10^6 Btu/hr = $(53.1 + 0.0142X)\ 10^6$ so X = 2,600 for polluting gases and our estimates for the major gases, in lb/hr and in tons/year. (Please note that the estimates apply to any incinerator, not just an incinerator made by IT Corporation.) Also, since we have estimated the total release of stack gas, we can calculate that this is 56,700 cubic meters per hour. From this number we have calculated the concentration of pollutants in the stack gas in micrograms per cubic meter.

TABLE 5-9 APPROXIMATE COMPOSITION OF THE STACK GAS FROM A SINGLE, 90 MILLION BTU/HR, INCINERATOR

	tons/yr	lb/hr	Concentration in the Stack ($\mu g/m^3$)
Nitrogen	473,000	108,000	
Carbon Dioxide	74,000	17,000	
Water Vapor	39,000	9,000	
Oxygen	74,000	17,000	
Carbon Monoxide	41*	9	72,000
Nitrogen Dioxide	70*	16	128,000
Hydrocarbons	17*	4	32,000
Sulfur Dioxide	63*	14	112,000
Hydrogen Chloride	18*	4	32,000
Particulates	70*	16	128,000

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*Estimated by IT Corporation. All other numbers estimated by WPA.

To understand the meaning of Table 5-9, the values given must be related to ambient air quality or to release rates from other sources. This is done in the following section. First, however, we attempt to relate the IT numbers to emissions from other types of facilities and, thus, to assess the validity of the numbers.

The quantity of carbon monoxide and nitrogen oxides released depends on the design of the incinerator, the temperature, the residence time and the excess air. There is very little dependence on the waste. Nitrogen oxides and carbon monoxide are formed during the process of combustion and are not removed in the gas cleaning section. The estimated quantities of carbon monoxide released are similar to the quantities released from other combustion processes and appear to be good estimates.

Preston and Miller, of the Electric Power Research Institute, (Reference 12), have discussed the formation of nitrogen oxides when coal is burned to generate electricity. Today's ordinary boiler gives 0.6 to 0.5 pounds of nitrogen oxides per million Btu in the coal. The best, most carefully controlled, modern boilers give 0.3 to 0.2 pounds of nitrogen oxides per million Btu in the coal. IT Corporation expects their incinerator to give 0.18 pounds of nitrogen oxides per million Btu in the waste. IT Corporation expects this low release of nitrogen oxides because the temperature of the waste incinerator will be lower than the temperature in a coal burning boiler. We also consider it to be important that the waste will contain less nitrogen than does coal. Most of the nitrogen oxides released are formed from nitrogen in the fuel (rather than nitrogen in the air). An important control must be to analyze incoming waste and to ensure that any waste with a high nitrogen content is diluted by waste with a low nitrogen content. If this is done the low rate of release of nitrogen oxides expected by IT Corporation will most probably be achieved.

Since about 10,000 lb/hr of wet waste which contains about 5,000 lb/hr of dry waste will be burned, the legal requirement for 99.99 percent destruction of waste gives a waste hydrocarbon emission of 0.5 lb/hr. A listed hydrocarbon emission of 4 lb/hr represents emission of hydrocarbons resulting from partial destruction of fuel and waste and not the original hazardous waste. An emission rate of 4 lbs/ hr. can be achieved.

Sulfur dioxide has a 50 percent content of sulfur and is more than 90 percent removed in the gas scrubber. A release rate of 14 lb/hr means a production rate of about 140 lb/hr, which would occur if the sulfur content of the fuel plus waste averaged about 0.7 percent. This is a reasonable expectation. However, we recommend that the incoming waste be analyzed and that any waste with a high sulfur content be diluted by waste with a low sulfur content.

Hydrogen chloride is formed from chlorine in chlorinated waste. Since at least 99 percent of the hydrogen chloride formed must be removed in the scrubber, a release of 4 lb/hr means a formation of 400 lb/hr. This implies an average chlorine content of the waste plus fuel of about

4 percent. In Section 7-6 in Table 7-1, we show that individual chlorinated compounds may have chlorine contents from 50 percent to 90 percent. But the chlorinated compounds going into the incinerator are usually well diluted with other, non-chlorinated wastes, because chlorinated wastes do not burn well. The release of hydrogen chloride is totally dependent on the mixture of waste received for incineration, and the amount shown on Tables 5-9 may be a conservatively high estimate.

The release rate of particulates is, unfortunately, sometimes expressed in the units of grains per dry standard cubic foot. One gr/dscf equals 2,300,000 $\mu g/m^3$ and we use only the units of $\mu g/m^3$. The release rates shown on Table 5-9 are regularly achieved in many industries (Reference 11). Another way of confirming the release rate is as follows. Particulates are at least 95 percent removed by scrubbing and up to 98 percent may be removed. The release of 16 lb/hr means the formation of at least 320 lb/hr of particulates, so at least 6.4 percent of the waste can be ash and form airborne particulates and still give the estimated release rate. The estimated release rate may be conservatively high.

5.5.3 The Effect of the Incinerator on Ambient Air Quality

One way to understand the effect of the incinerator is to compare it to an automobile. When an automobile is driven one mile the average emissions from the exhaust are those listed on Table 5-10. Therefore, we can say approximately that:

> the emission of nitrogen oxide from the incinerator is equivalent to the emissions from 4,000 automobile miles per hour;
>
> the emission of carbon monoxide from the incinerator is equivalent to the emissions from 150 automobile miles per hour;
>
> the emission of hydrocarbons from the incinerator is equivalent to the emission from 670 automobile miles per hour.

A figure of 4,000 automobile miles per hour can be understood as 400 cars driving 10 miles through a town each hour or 100 cars driving around and around at 40 miles per hour. The Massachusetts Turnpike carries an average of 10,000 vehicles per day in each direction which is an average of 833 cars per hour in two directions. The traffic on five miles of turnpike, therefore, averages 4,000 automobile miles per hour.

TABLE 5-10 AVERAGE EMISSIONS FROM AN AUTOMOBILE EXHAUST FOR ONE MILE OF DRIVING

	Old Vehicles		New Vehicles		Assumed for Mixture of Vehicles
	lb.	grams	lb.	grams	lb
Nitrogen Oxides	0.009	4	0.002	1	0.004
Carbon Monoxide	0.20	90	0.02	10	0.06
Hydrocarbons	0.02	9	0.002	1	0.006

The second way to understand the effect of the incinerator is to determine the effect on ambient air quality. However, this is not straightforward. The gases pass up a tall stack and are distributed and diluted by the atmosphere. Accurate estimates require knowledge of the terrain and the wind direction and velocity. Fortunately the EPA has determined, based on much experience, that an emission of 1 ton/year (= 0.23 lb/hr) will cause, on the average, less than 0.5 $\mu g/m^3$ increase in ambient air concentration. This is the maximum increase in ambient concentration and can be used for all the gases except nitrogen oxides. Nitrogen oxides increase at only 1/5th of this rate, probably because they are fertilizers and are rapidly withdrawn from the atmosphere by plants.

TABLE 5-11 APPROXIMATE INCREASE IN AMBIENT CONCENTRATION DUE TO EMISSIONS FROM AN INCINERATOR

	Emission (tons/yr)	Increase in Ambient Concentration ($\mu g/m^3$)	Range of Background Ambient Concentration ($\mu g/m^3$)
Carbon Monoxide	18	9	60-1200
Nitrogen Oxides	70	7	40-80
Hydrocarbons	17	9	70-100
Sulfur Dioxide	63	32	25-340
Hydrogen Chloride	18	9	N/A*
Particulates	70	35	10-200

---

*Not usually measured, very low.

On Table 5-11 are listed the emissions from Table 5-9, the approximate increase in ambient concentration caused by these emissions, and the background ambient concentration range to which the increase should be compared. The increase does not make the ambient air unhealthfull in any case, but does contribute importantly to the ambient concentration of sulfur dioxide and particulates.

5.6 Sludge Dewatering

Before burning wet sludges, it may be worthwhile removing some water so as to economize on fuel in the incinerator. Water can be squeezed out of organic sludges by pushing the sludge on moving belts between rollers. Other equipment for dewatering includes vacuum filters and filter presses. The water will be dirty and must be sent to water treatment.

5.7 Crushing Solid Wastes

Some solid wastes must be crushed to ensure complete vaporization in the rotary kiln. The crushing must be done in such a way as to avoid vapors, odors, spills and splashes.

5.8 Monitoring

In their Notice of Intent, IT Corporation (Reference 8) have elected to monitor ambient air at three sites, one close to the facility and two downwind from the facility. Analysis will be done for nitrogen oxides, sulfur dioxide and particulates. Our analysis in Section 5.5.3 is in agreement that these are the most important pollutants.

However, sampling and analysis of the stack gas from within the stack is the essential means of controlling the incinerator. We particularly recommend continuous analysis where this is possible. Remember that stack gases are continuously released as they are formed. It is possible to change incineration conditions by switching from waste to fuel quite rapidly once excessive toxic gases have been detected, so it is necessary to detect any excessive release as soon as possible after it starts. Continuous analyzers are available for carbon monoxide, nitrogen oxides, hydrocarbons, sulfur dioxide and particulates. These are discussed below.

Continuous analyzers are not available for specific organic compounds. For this reason a comprehensive program of sampling and analysis must be made whenever a new type of waste is being burned. In addition, analyses of samples must be made periodically whenever the incinerator is in use. The period between analyses will depend on the experience with the particular waste being burned.

Continuous analyzers can be obtained with EPA certification. Certification means that the manufacturer has used the tested and approved design and conducted all necessary quality checks. It also means that the instrument has been recalibrated and recertified at required intervals of use. An up-to-date certification is a useful check on the quality of the monitoring. The principles of continuous analyses are given below.

Carbon Monoxide. Carbon monoxide is detectable in the parts per million level (thousands of $\mu g/m^3$) by its ability to absorb infrared radiation.

Nitrogen Oxide, (NO) This gas reacts with ozone to give a molecule which emits infra-red radiation which can be detected. Ozone is generated and mixed with some stack gas which is drawn through the instrument. The principle is called "chemiluminescence." Parts per billion (single number of $\mu g/m^3$) can be detected. Nitrogen dioxide (NO_2) can also be measured. Nitrogen dioxide is converted to nitrogen oxide (NO) by passing the gas over a hot metal catalyst. It is the nitrogen oxide which is then detected.

Hydrocarbons. Hydrocarbon molecules will ionize in a hot flame such as is caused by burning hydrogen in oxygen. If two electrodes are placed one on either side of the flame, the ionization is detected by an increased electrical current. This technique, called "flame ionization" detects hydrocarbons in the parts per million level (hundreds of $\mu g/m^3$).

Sulfur Dioxide. Two methods are used to measure sulfur dioxide. Either ultraviolet light is passed through the gas, or the gas is heated in a very hot flame which can be the same flame as used for hydrocarbon measurement. In either case the sulfur dioxide in the gas is caused to emit a detectable radiation which can be used to measure the concentration down to low levels.

Hydrogen Chloride. There is no simple method to continuously analyze for hydrogen chloride. Sampling and batch analysis is required.

Particulates. Continuous analysis of particulates can be done by light scattering or similar measurements. We have not found a source for a certified analyzer. The usual practice is to sample continuously and weigh the collected solids at intervals.

A survey of available instruments for continuous stack gas monitoring has been published in an April, 1982 publication of the Instrumentation Society of America (Reference 13). Table 5-11 has been taken from Reference 13.

5.8.1 The Consequence of Failure

If monitoring shows excessive pollutants in the stack gas, then incineration conditions must be altered, by switching from waste to fuel, quickly. As incineration is a rapid process, changes in conditions will alter the stack gas, in a few minutes. Adequate monitoring can ensure that excessive pollutants are not released.

5.9 Summary of Recommendations for Monitoring and Control of a Waste Incinerator

Throughout this section we have made certain recommendations which we summarize here. Our recommendations are concerned with:

Analysis of the waste fed to the incinerator,
Control of the incineration,
Monitoring of the incinerator stack gas.

These areas of importance are illustrated in Figure 5-9.

Analysis and Monitoring

Periodically sample and analyze the incoming waste to detect unallowed toxic materials or excessive concentrations of sulfur or nitrogen.

Continuously monitor the stack gas for nitrogen oxides, carbon monoxides, sulfur dioxide, hydrocarbons.

Continuously monitor the stack gas for an increase in particulate content.

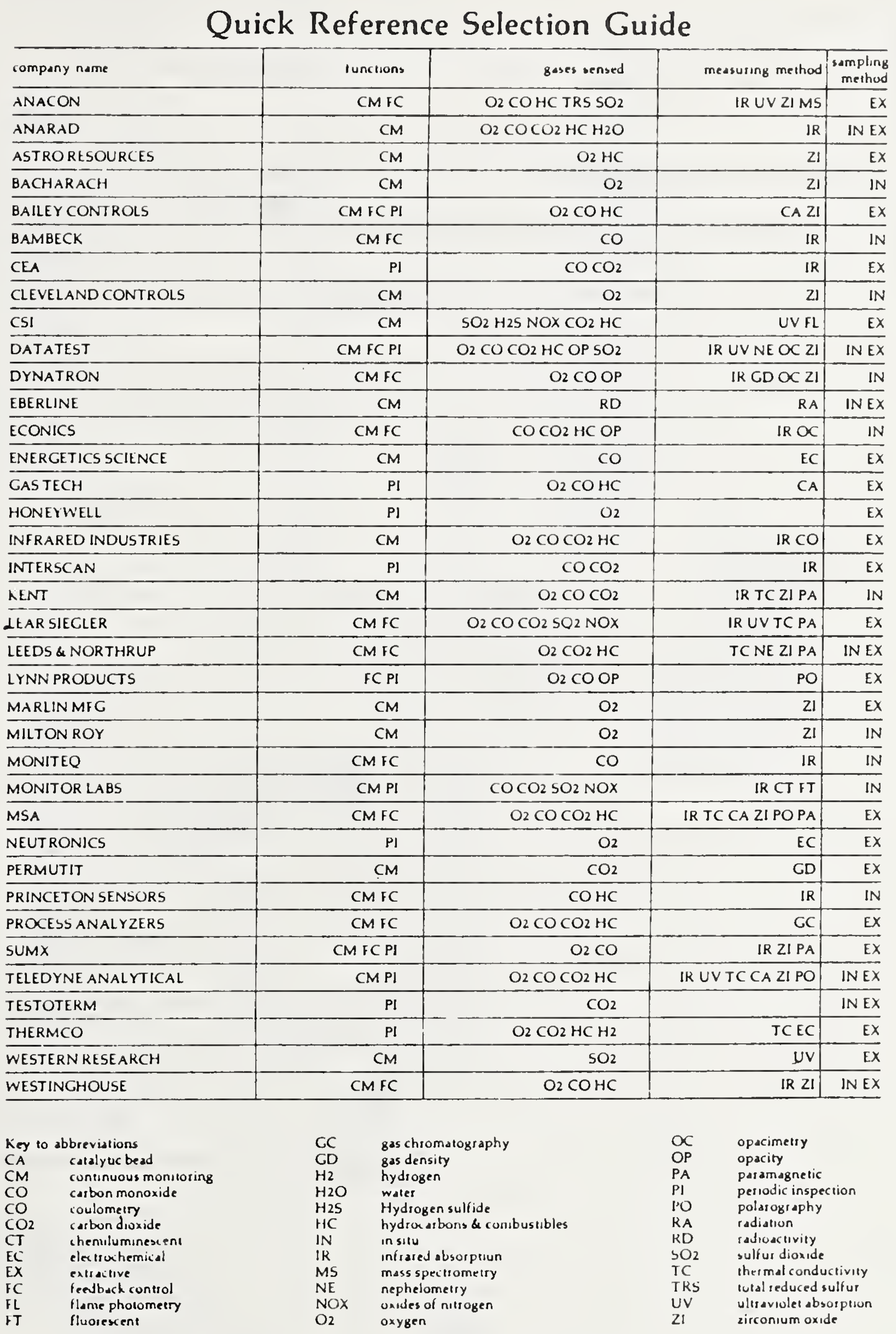
Periodically sample and analyze the stack gas for specific toxic compounds and particulate content.

Periodically sample and analyze the scrubber wastewaters for metals.

Controls

Control of residence time, temperature and air flow in incineration to ensure acceptable levels of carbon monoxide, nitrogen oxides and hydrocarbons emitted in the stack gas.

TABLE 5-12. AVAILABLE INSTRUMENTS FOR CONTINUOUS STACK GAS MONITORING*



Quick Reference Selection Guide

company name	functions	gases sensed	measuring method	sampling method
ANACON	CM FC	O_2 CO HC TRS SO_2	IR UV ZI MS	EX
ANARAD	CM	O_2 CO CO_2 HC H_2O	IR	IN EX
ASTRO RESOURCES	CM	O_2 HC	ZI	EX
BACHARACH	CM	O_2	ZI	IN
BAILEY CONTROLS	CM FC PI	O_2 CO HC	CA ZI	EX
BAMBECK	CM FC	CO	IR	IN
CEA	PI	CO CO_2	IR	EX
CLEVELAND CONTROLS	CM	O_2	ZI	IN
CSI	CM	SO_2 H_2S NOX CO_2 HC	UV FL	EX
DATATEST	CM FC PI	O_2 CO CO_2 HC OP SO_2	IR UV NE OC ZI	IN EX
DYNATRON	CM FC	O_2 CO OP	IR GD OC ZI	IN
EBERLINE	CM	RD	RA	IN EX
ECONICS	CM FC	CO CO_2 HC OP	IR OC	IN
ENERGETICS SCIENCE	CM	CO	EC	EX
GAS TECH	PI	O_2 CO HC	CA	EX
HONEYWELL	PI	O_2		EX
INFRARED INDUSTRIES	CM	O_2 CO CO_2 HC	IR CO	EX
INTERSCAN	PI	CO CO_2	IR	EX
KENT	CM	O_2 CO CO_2	IR TC ZI PA	IN
LEAR SIEGLER	CM FC	O_2 CO CO_2 SO_2 NOX	IR UV TC PA	EX
LEEDS & NORTHRUP	CM FC	O_2 CO_2 HC	TC NE ZI PA	IN EX
LYNN PRODUCTS	FC PI	O_2 CO OP	PO	EX
MARLIN MFG	CM	O_2	ZI	EX
MILTON ROY	CM	O_2	ZI	IN
MONITEQ	CM FC	CO	IR	IN
MONITOR LABS	CM PI	CO CO_2 SO_2 NOX	IR CT FT	IN
MSA	CM FC	O_2 CO CO_2 HC	IR TC CA ZI PO PA	EX
NEUTRONICS	PI	O_2	EC	EX
PERMUTIT	CM	CO_2	GD	EX
PRINCETON SENSORS	CM FC	CO HC	IR	IN
PROCESS ANALYZERS	CM FC	O_2 CO CO_2 HC	GC	EX
SUMX	CM FC PI	O_2 CO	IR ZI PA	EX
TELEDYNE ANALYTICAL	CM PI	O_2 CO CO_2 HC	IR UV TC CA ZI PO	IN EX
TESTOTERM	PI	CO_2		IN EX
THERMCO	PI	O_2 CO_2 HC H_2	TC EC	EX
WESTERN RESEARCH	CM	SO_2	UV	EX
WESTINGHOUSE	CM FC	O_2 CO HC	IR ZI	IN EX

Key to abbreviations

CA	catalytic bead
CM	continuous monitoring
CO	carbon monoxide
CO	coulometry
CO_2	carbon dioxide
CT	chemiluminescent
EC	electrochemical
EX	extractive
FC	feedback control
FL	flame photometry
FT	fluorescent
GC	gas chromatography
GD	gas density
H_2	hydrogen
H_2O	water
H_2S	Hydrogen sulfide
HC	hydrocarbons & combustibles
IN	in situ
IR	infrared absorption
MS	mass spectrometry
NE	nephelometry
NOX	oxides of nitrogen
O_2	oxygen
OC	opacimetry
OP	opacity
PA	paramagnetic
PI	periodic inspection
PO	polarography
RA	radiation
RD	radioactivity
SO_2	sulfur dioxide
TC	thermal conductivity
TRS	total reduced sulfur
UV	ultraviolet absorption
ZI	zirconium oxide

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*_Instrumentation Technology_, p. 33, April 1982.

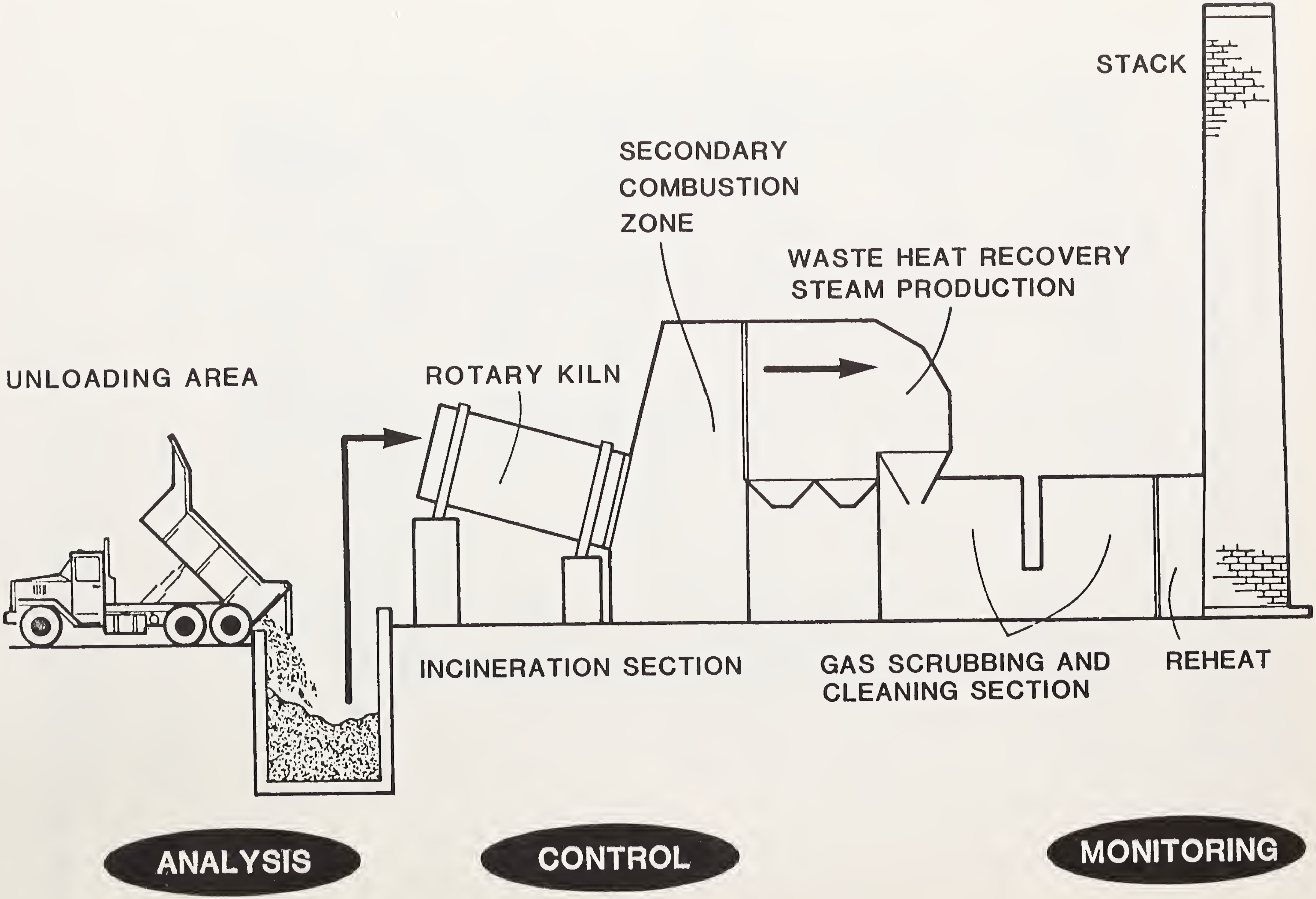
UNLOADING AREA
ROTARY KILN
SECONDARY COMBUSTION ZONE
WASTE HEAT RECOVERY STEAM PRODUCTION
STACK
INCINERATION SECTION
GAS SCRUBBING AND CLEANING SECTION
REHEAT
ANALYSIS
CONTROL
MONITORING

Figure 5-9. Recommended monitoring and control of a waste incinerator.

Installation of gas scrubbing and particulate removal equipment adequate to reduce sulfur dioxide, hydrogen chloride and particulates to acceptable levels.

Installation of alarms and automatic shut down controls if excessive pollution detected in stack gas.

Operation

If excessive pollution is detected in the stack gas, sound the alarm, make immediate correction and/or shut down the system for repair.

If excessive metals are detected in wastewater, analyze and segregate the waste.

If excessive sulfur or nitrogen is found in the waste, dilute before burning.

6. SOLVENT RECOVERY

6. SOLVENT RECOVERY

Some wastes sent to the hazardous waste treatment facility should be recovered. The wastes for which recovery is always the first consideration are solvents. Probably most of the solvents received for recovery will come from paint manufacturing and leather tanning. These solvents will contain pigments and materials called resins which bind the pigment and add the gloss to painted surfaces and treated leather. Other examples are dry cleaning liquids from cleaning clothing and degreasing liquids from cleaning metal parts in machine shops. These wastes are more than 90 percent reusable solvent. But they are contaminated with the grease and dirt that dissolved in them during use, and often water has dissolved in them.

If solvent extraction (described in Section 7.7) is used to treat wastewater in the hazardous waste facility, this will be another source of dirty solvent which needs recovering.

Recovery is accomplished by distillation.

6.1 Distillation

Distillation is the process by which chemical compounds are separated by virtue of their volatility, or ease with which they can be vaporized. If a typical dirty solvent is placed in a pot and heated so that it boils, the vapor which leaves is solvent with no dirt or grease and very little water. As solvent leaves, the dirt in the waste solvent in the pot becomes more concentrated and the boiling temperature rises. When enough solvent has left, the boiling temperature rises to the temperature of boiling water, and the vapor now contains a lot of water. When nearly all the liquid, solvent and water, has been boiled off, the residual material in the pot becomes viscous (sticky, thick) and boiling is no longer possible. The residue, which is a type of sludge, can be incinerated. Or, it can be transferred to a different type of equipment, called a wiped film evaporator (see Section 6.4), for additional recovery of solvent.

Heating is done with steam. A coil, like a house radiator, is placed within the solvent in the pot. Steam condenses and gives off heat. Condensed steam (water) is returned to the boiler. The process of heating produces no fumes and cannot start a fire. However, the hot solvent in the process is highly flammable and if the distillation pot ruptures, spilling out solvent, the solvent can catch fire from a spark or other flame source.

The vapor leaving the pot is condensed. A condenser is pictured in Figure 6-1. A condenser is a bundle of tubes through which cold water is passed to keep the outer surface cold. The tubes are kept separated by spacers and enclosed in a cylindrical steel shell. Vapor from the distillation pot passes into the shell, is cooled on the cold, outer surfaces of the tubes and condenses or liquifies. The liquid, recovered solvent runs out to a storage container. A vapor line from the condenser shell is connected to the incinerator. The vapor line has an exhaust fan and ensures that fumes do not escape.

If a simple pot and condenser are used, the condensed liquid is sent to solvent storage during the first part of the distillation and to dirty water storage during the second part of the distillation.

A better separation of solvent and water can be obtained if a still column is used. A simplified version is pictured in Figure 6-2. A still column is a vertical steel pipe filled with specially shaped pieces of ceramic whose dimensions vary from 1/2 to 2 inches. Waste solvent is poured down the column while vapor from the still pot rises up the column. The vapor repeatedly condenses on the liquid giving up heat and causing fresh vapor to form. As the vapor is condensed and revaporized its composition changes; the solvent vapor becomes purer as it approaches the top of the column.

The distillation equipment shown in Figure 6-2 is designed to be used on a single batch of waste at one time. Water and sludge accumulate in the pot until the batch of waste is used up. Then the water can be boiled off. It is, however, common to run the still continuously. Waste solvent is poured down the column. Solvent is removed continously from the top of the column, water is removed continously from an opening in the middle of the column where a second condenser is provided and residual sludge is removed continuously from the pot.

6.1.1 Performance and Reliability

Distillation is the most important method of separating and purifying organic chemicals. Oil refineries and all organic chemical manufactur-

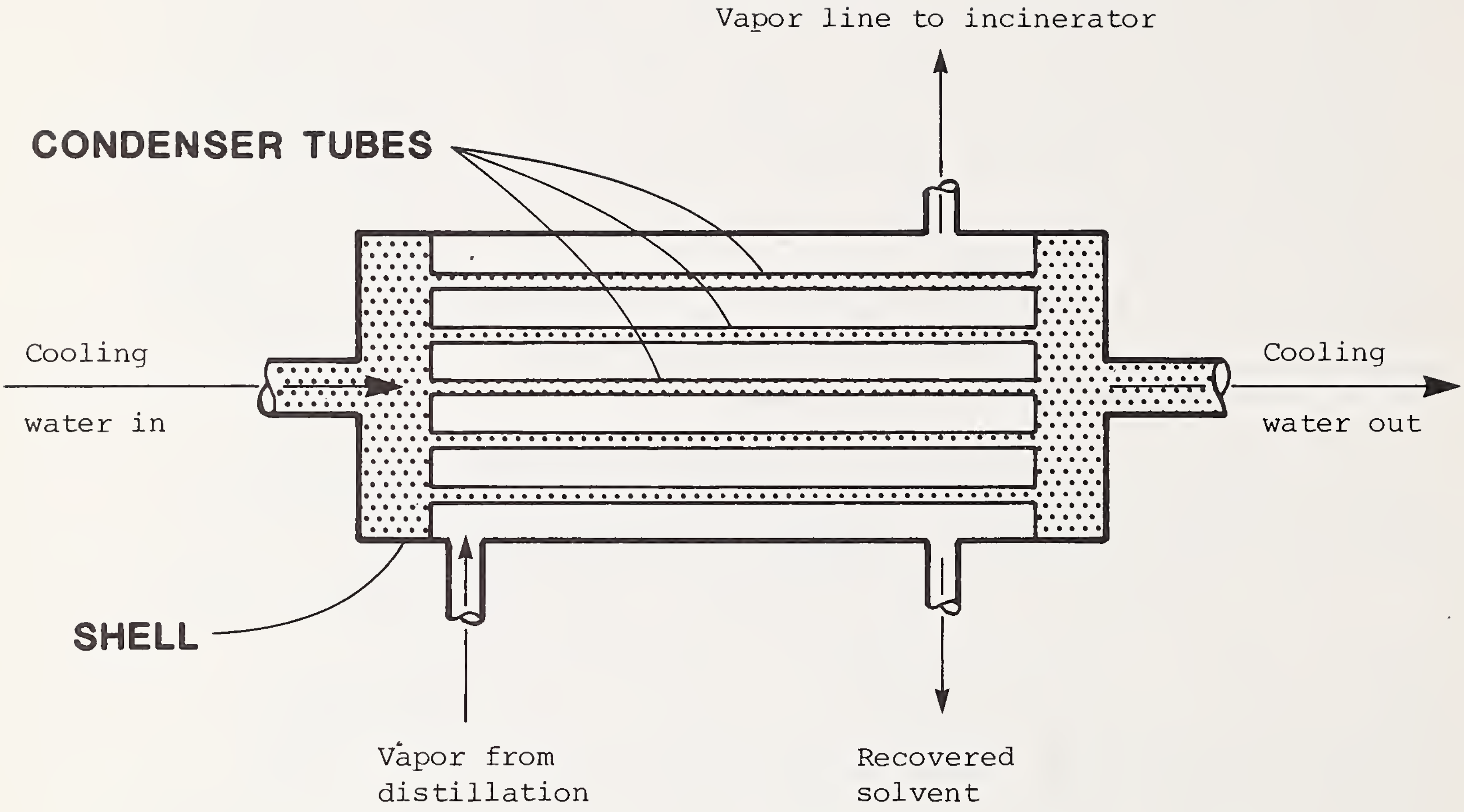

Figure 6-1. Condenser.

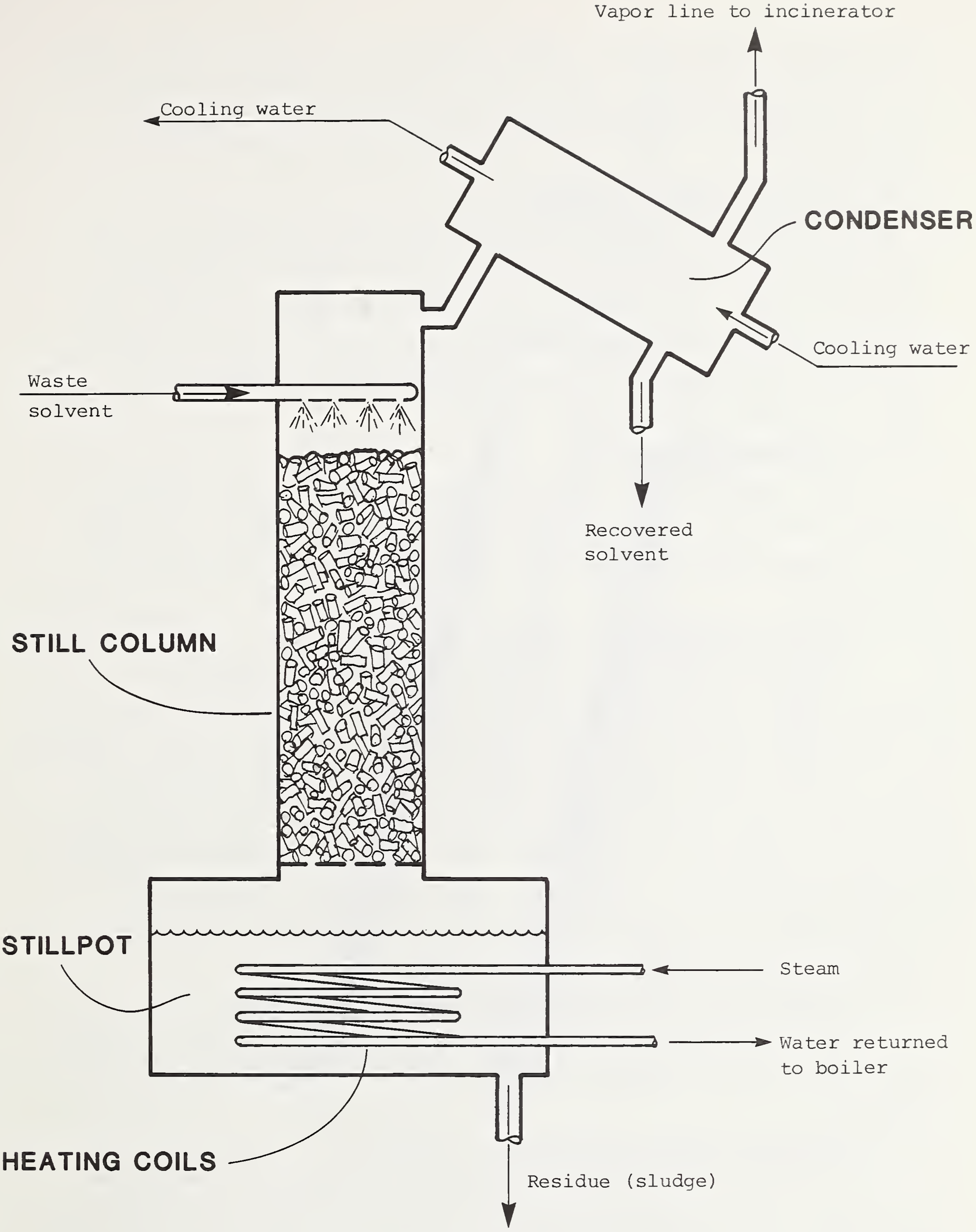

Figure 6-2. Distillation equipment.

ing depend on distillation. Design and operation of distillation columns are standard and reliable. Also, if the column is off-duty for repair or any other reason, the waste solvent can simply be held in storage or incinerated.

6.2 Prevention of Vapor Emissions

The colder the condenser the lower the vapor emission rate. For this reason the condenser will be water cooled, not air cooled, and be generous in size. All vents will go to the incinerator or other flame and will have exhaust fans so they are just below atmospheric pressure. This means that any leaks will be air leaking into the duct and not vapor leaking out of the duct.

6.3 Handling Water Emissions

Water recovered in a solvent still will not be fit for discharge. The water must be held in covered storage tanks and treated. The water may be steam stripped and may need other treatment such as biological oxidation.

6.4 Additional Recovery by a Wiped Film Evaporator

A diagram of a wiped film evaporator is shown in Figure 6-3. Thick, viscous residue from the still pot or as received by the facility is put into a cylinder which is heated from the outside by steam condensing in a jacket. Wiper blades on a central shaft are rotated continously. The blades catch the material as it is fed and wipe it into a thin film on the hot surface of the cylinder. The heat causes solvent to vaporize. The vapor leaves and is condensed. The wiper blades sweep the semi-solid residual concentrate to an exit port where it drops out of the evaporator and is carried to the incinerator.

6.5 Incineration of Sludge and Other Useless Combustibles

Sludge and other useless combustibles will be incinerated. Landfill will not be used for organic residues. Incineration is described in Section 5.

6.6 Shipping Out Recovered Solvent

Recovered solvent will be shipped out of the plant in tank trucks or barrels. The procedures and safety precautions must be the established procedures used in the original manufacturing plant and in the users' plant.

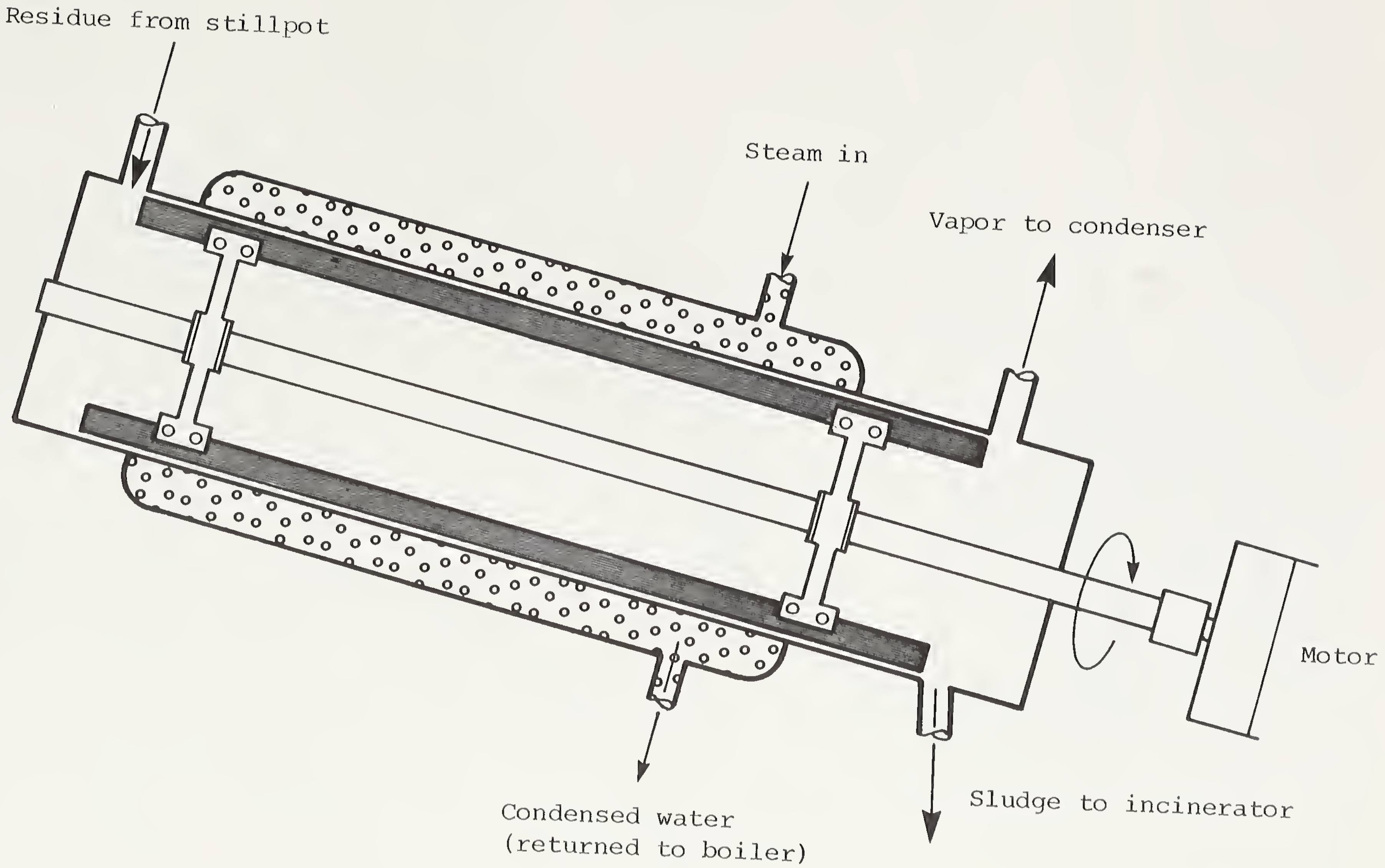

Figure 6-3. A wiped film evaporator.

6.7 Monitoring

Liquids and sludges are held in tanks and analyzed, should this be required, before incineration or shipping out. Vapor leaks can be detected by means of a continuous hydrocarbon analyzer placed in the same room as the still. Such analyzers are described in Section 5.

6.7.1 The Consequence of Failure

If a vapor leak is detected, distillation must be stopped by stopping the flow of heating steam to the still.

If distillation is inadequate because the quality of the recovered solvent is insufficient, the solvent can be redistilled or incinerated.

7. WASTEWATER TREATMENT

7 WASTEWATER TREATMENT

7.1 Introduction

Although wastewaters can be incinerated, incineration is not necessarily the best treatment. There are two problems. When large amounts of water are put into the incinerator, a lot of valuable fuel is used to boil the water. Also, when water boils, salts and other non-combustible materials which were in solution, form a very fine, dusty solid which sweeps out of the incinerator in the gas. This dust can be removed in the scrubbing and cleaning section, but this puts a heavy load on the equipment.

Wastewaters that are heavily contaminated with combustible waste that is not worth recovering will often be incinerated. But for most wastewaters, alternative treatments will be considered. Approximately 6 percent (60,000 parts per million (ppm)) of organic waste in water will provide enough heat to vaporize the water. But even with this concentration, fuel will be needed to complete the incineration.

A key to understanding water treatment is that the various different treatments are quite specific. A single treatment will usually remove only one type of contamination. Each wastewater must be analyzed to find the nature of the contamination. The most important classifications of contaminants are:

Oil or Undissolved Organic Liquids
Metals
Acids or Alkalis
Chlorides
Organics (as measured by total organic carbon or similar test)

If the water contains any of these types of contamination it must be treated separately for each type. Wastewater will often pass through several treatments in sequence.

Suspended solid particles are an additional type of contamination that we have not listed separately because suspended particles are removed in many of the treatments designed to remove other contaminants.

On Figure 7-1 is shown one possible sequence of treatments for wastewater. Please note that many different sequences are possible

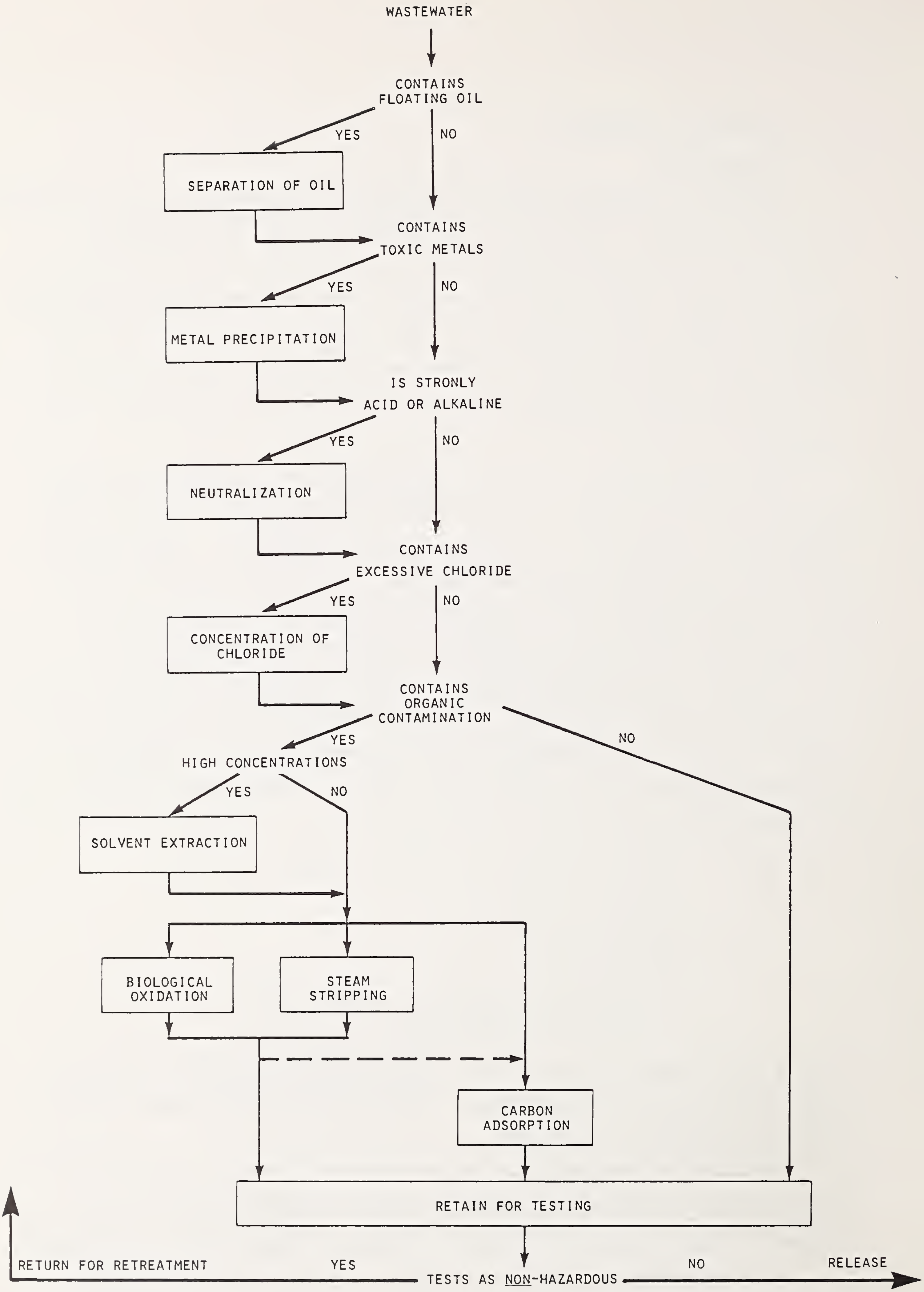

Figure 7-1. Choice of wastewater treatment.

and that Figure 7-1 shows only one possibility. Figure 7-1 will become more understandable as we discuss each individual treatment in turn.

An important point, shown in Figure 7-1, is that all treated water must be retained and analyzed. Treated water may be released in batches only after it has been fully tested and found to be non-hazardous. This is discussed more fully in Section 7-13.

7.2 Oil and Water Separation

Oil does not mix with water and can usually be removed because it floats to the top or sinks to the bottom. Suspended particulates can be settled in the same settling tanks. Sometimes, however, very small droplets of oil form in the water and do not coagulate or clump together. When this happens, the oil remains suspended in the water and will not separate. A suspension of very fine droplets is called an emulsion. Usually there is a chemical in the water which is like a detergent. This chemical surrounds the droplets of oil and gives them a small electrical charge on the surface. The electrical charge repels other droplets and coagulation does not occur. A chemical with an opposite charge can often be added to break the emulsion and cause the oil to coagulate. Also, simply heating will often break the emulsion.

Quality of Treated Water

Residual oil left in the water after separation is usually in the range of 10 to 50 ppm.

Emissions

Separation gives an oily layer with a little water in it, a water layer with very little oil left in it and sometimes a sludge at the bottom of the tank. Vapor emissions do not occur, providing heat is not used on a wastewater with a particularly volatile contamination.

7.3 Treatment for Metals and Cyanide

Wastewater from electroplating shops is typical of this category, but other wastewaters may also require metal removal. The electroplating waste comes from spent plating baths and from the water used to rinse the metal parts after they have been plated. The most common contaminants are copper, nickel, zinc, and chromium. Cyanide is also often present, dependent on the type of plating solution used.

Treatment of this type of wastewater has been a standard procedure for many years. Details of the chemistry are given in textbooks, for example References 4 and 5. However, chemical details are not needed to understand the nature of the emissions. Incineration is not a useful treatment for this water. The proper practice is to alter the form of the dissolved metals and precipitate them as insoluble solids which can safely be used for landfill. In a hazardous waste facility, the wastewater will usually be treated in batches in big stirred tanks by adding the appropriate chemicals and allowing time for the chemical reactions to occur. It will take several hours to treat a batch. Vapor emissions are negligible and the tanks may have loose covers or be open-topped. Heat is not required.

If cyanides are present, they must be destroyed by sodium hypochlorite (which is a concentrated form of household bleach) and caustic soda. Chromium will usually have to undergo a chemical reaction called "reduction" by adding sodium bisulfite and sulfuric acid. Special metals may require a treatment specifically designed for that metal. Patterson (Reference 4) provides a complete list of possibilities. But most metals can be removed from solution by adding lime, which causes the metal to precipitate as its oxide or hydroxide.

Metals are not usually found in nature in their metallic form. Metals are mined in a combined state which is called an ore. Smelting processes are used to separate pure metal from the ore. Many ores are metal oxides, and the precipitate formed by adding caustic soda to wastewater is related to natural ores. The precipitate will be separated from the water by allowing it to settle in tanks, basins or lined lagoons. As the water is drawn off the top of the precipitate, it will be filtered to remove the last traces of solid. The filtered water will be neutralized and may then require additional treatment as listed on Figure 7-1.

The precipitated solids are dewatered and then stabilized as described in Section 8.2.

Quality of Treated Water

Lancy Laboratories (Reference 6) finds that precipitation treatment varies with the care taken in the operation. All metals that can be precipitated, and cyanide, must always be reduced to below 1 ppm.

Careful operation and control can, if the waters were not mixed before receiving them for treatment, reduce cyanide to 0.1 ppm, chormium to 0.25 ppm, cadmium and lead to 0.1 ppm.

Emissions

Most wastewaters requiring precipitation treatment will not contain volatile organic chemicals and will not produce vapor emissions. In the exceptional case, the waste should be steam stripped first. The precipitation treatment does not need equipment to contain vapors.

The sludge which results from the solid metal oxides must be "stabilized" or rendered nonleaching before being sent to landfill. The hazardous waste treatment plant will probably receive, for stabilizing and landfill, additional metal sludges from electroplating shops who do their own precipitation and prefer to ship out sludge instead of wastewater. Stabilization is described in Section 8.

7.4 Neutralization

Precipitation treatment must be followed by neutralization. Water is close to neutral, but strong acids and strong bases (or alkalis) are not neutral, are corrosive and, therefore, hazardous. Neutralization consists of adding acid (sulfuric acid) to basic wastes or alkali (lime) to acid wastes. Neutralization is a simple, standard procedure, easily instrumented and controlled. However, neutralization results in the formation of a salt, and disposal of the salt residue requires careful consideration.

To precipitate metals, as described above, the solution is usually made alkaline with lime which is calcium hydroxide. After the precipitated metals have been filtered off, the alkaline water will be neutralized with sulfuric acid. Neutralization results in the formation of the insoluble salt calcium sulfate. Calcium sulfate is gypsum. It is the material which forms when plaster of Paris hardens. Most interior house walls are made of calcium sulfate. Calcium sulfate is colorless and non-toxic. It is also insoluble and precipitates. Precipitated calcium sulfate can be allowed to settle or is filtered off. Calcium sulfate does not redissolve in acid rain. This material can safely be landfilled in a non-secure landfill.

The hazardous waste treatment facility will not only be neutralizing solutions as part of other treatments, it will receive wastes specifically requiring neutralization. Most of the incoming, non-neutral wastes will be acids. Examples are battery acids, steel pickling acids and waste acid from jewelry and other metal cleaning and refining. Acids will be neutralized by lime, and salts of calcium will be formed. Depending on the acid neutralized, the calcium salt will precipitate or remain in solution.

Sulfuric acid yields precipitated calcium sulfate
Hydrofluoric acid yields precipitated calcium fluoride
Hydrochloric acid yields soluble calcium chloride
Nitric acid yields soluble calcium nitrate

Precipitated calcium salts can be settled or filtered off and landfilled. Calcium chloride is discussed in the next section. Not a lot of nitrate is expected from a hazardous waste facility but a brief discussion is given in Section 7-6.

The largest quantity of waste expected in the facility is used pickling acid from steel working. Some of this acid may be sulfuric acid, but most will be hydrochloric acid which, on neutralization, will form soluble calcium chloride. Also, steel pickling acid will contain quantities of iron which, upon neutralization (and bubbling air through the solution) will precipitate as iron hydroxide (ferric hydroxide). Ferric hydroxide is common rust. It is a brown, insoluble substance that is non-toxic. It can be settled or filtered-off and safely landfilled. Iron precipitates out from neutral water; it is not necessary to make the water alkaline. If, however, other metals are present, after filtering the iron the other metals may be precipitated by adding extra lime as described above in Section 7.3.

Quality of Treated Water

Neutralized water should be controlled through pH measurement to be adequately and safely neutral. Soluble salts, particularly calcium chloride, will remain in the water. Organic matter originally in the water is usually not altered by neutralization.

Emissions

Neutralization may result in a sludge of iron oxide and calcium sulfate. The sludge can be landfilled.

7.5 Treatment for Chlorides

The most important wastewater in this category is used water from scrubbing incinerator gases. When "chlorinated" wastes are burned, all the chlorine is converted to the acid gases hydrogen chloride plus a little chlorine. Hydrogen chloride and chlorine are scrubbed out of the incinerator gas by water. The acid which results is usually neutralized with lime to produce calcium chloride. Calcium chloride is very soluble and remains in the water. A few numbers will help to determine whether the chloride formed this way is a problem.

On Table 7-1 is shown the chlorine content of several common chlorinated chemicals. As an example, suppose that the facility receives one ton of mixed organic waste containing 50 percent chlorine. One ton (2,000 lb) of waste yields 1,000 lb of chlorine which, after being converted to calcium chloride, becomes 1,560 lb of calcium chloride. Continuing the example, suppose that the calcium chloride ends up as a one percent solution in used scrubber water. One ton of waste will cause 19,000 gallons of waste scrubber solution.

TABLE 7-1. WEIGHT PERCENT CHLORINE IN SOME SIMPLE CHLORINATED CHEMICALS

	Weight Percent Chlorine
Vinyl Chloride	57
Methylene Chloride	70
Dichloroethane	72
Dichloroethylene	73
Chloroform	89
Carbon Tetrachloride	92

We must emphasize that continuous incineration of waste containing 50 percent chlorine is not expected. The average chlorine content of the waste being incinerated is probably below three percent.

In addition to the chloride in scrubber water, chloride will be shipped into the plant as dirty hydrochloric pickling acid requiring neutralization as described in Section 7-4.

Given a knowledge of how much chlorinated waste is going to be incinerated, a decision can be made as to whether or not the chloride produced can be accepted and carried away by the local river.

If the local river cannot accept the chloride, it must be disposed of in some other way. Disposing of chloride, instead of discharging it to a river, is not usually practiced but there are three possibilities which could be investigated. It may be possible to recover hydrochloric acid. Instead of neutralizing the scrubber water, it is boiled. When a dilute solution of hydrochloric acid is boiled, the vapor is pure water which can be condensed and reused for scrubbing. This process must be monitored so that no hazardous vapors are released by boiling, but release is not likely. The concentrated hydrochloric acid which remains, if clean, can be sold. The most important use will be pickling or cleaning steel in a steel mill.

Alternatively the scrubber water can be neutralized and the resulting solution of calcium chloride may be solidified to stabilize it against leaching, or it may be recovered. Calcium chloride from neutralization of waste hydrochloric acid may also be disposed of in the same ways. Cement will harden in the presence of calcium chloride, and a very high fraction of the chloride will remain in the cement and not leach out. Calcium chloride is very often added to cement kilns during the manufacture of cement. A concentrated solution of calcium chloride will suffice, it is not necessary to produce a dry solid.

Whether calcium chloride is solidified in cement or usefully used in a cement kiln, the water solution must be concentrated. Concentrating treatments are given the name "desalination". On Table 7-2 are given a few details about four possible processes. Please note that the numbers on Table 7-2 are all approximate.

In reverse osmosis, water is forced through a selective membrane under pressure. A high pressure pump is needed. The membrane will prevent most of the salt from passing.

In electrodialysis, the salt in solution, which is electrically charged, is transported by an electrical current. One-way membranes allow the salt to leave but prevent it from returning.

In a vapor compression evaporator, the water is boiled away leaving the salt behind. The steam leaving is compressed and condensed in tubes below the surface of the water which supplies heat to boil away more water.

In a single or multi-effect evaporator, the water is also boiled

TABLE 7-2. METHODS OF DESALINATION

Name	Form of Energy Used	Performance (Ratio 1)	Approximate Concentration of Salt in the Clean Water for 1% Feed (parts per million)	Approximate Concentration of Salt in the Concentrated Waste (percent)
Reverse Osmosis	Electricity or other mechanical drive	70 to 80	about 400 ppm	2 to 5%
Electrodialysis	Electricity	about 20 (for a 1% feed)	can be controlled, about 400 ppm	can be controlled up to 10%
Vapor Compression Evaporation	Electricity or other mechanical drive	about 9.5	very low 1 to 10 ppm	20 to 30%
Single or Multi-Effect Evaporation	Steam	1 to 4	very low 1 to 10 ppm	20 to 30%

NOTES:

(1) Performance ratio is the pounds of clean water recovered for the expenditure of 1,000 BTU of heat or 0.1 kw-hrs of electrical energy. 1,000 BTU is the heat needed to boil 1 pound of water. An electrical generating station consumes about 10,000 BTU to generate 1 kw-hr. More efficient processes have higher performance ratios.

away leaving the salt behind. But the source of energy is steam from a boiler instead of an electrically driven compressor.

Probably a waste treatment facility will try to use a single or multi-effect evaporator using steam produced from heat from the incinerator. This source of energy is cheap. If there is not enough steam, the highly efficient reverse osmosis system can be used to remove half the water (and concentrate the salt from 1% to 2%), with the concentrated solution from the reverse osmosis being further concentrated in a steam driven evaporator.

The quality of the clean water from a reverse osmosis unit may not be very important. It may be possible to reuse the clean water in the scrubber and not discharge it.

Quality of Treated Water

The approximate concentration of salt in the treated water depends on the desalination processes. Estimates are shown in Table 7-2.

Emissions

The major emission is a concentrated solution of calcium chloride. This must be disposed of by solidification or use as discussed above.

Organic matter in the salty water will probably end up in the cleaned water because it boiled away with the water in the evaporator. If too much organic matter accumulates, part of the water must receive a general organic removal treatment such as biological oxidation (Section 7.9) or carbon adsorption (Section 7.10) before reuse.

7.6 Treatment for Nitrate

As we mentioned, not a lot of nitrate is expected from a hazardous waste facility. Nitrate is a plant nutrient or fertilizer. Nitrate sometimes gets into a river when rain runs off a recently fertilized field or piles of animal waste. Nitrate causes green growth and does not survive in the water. Destruction of nitrate by natural growth of plants is the best way to dispose of it. However, excessive growth can choke a river with weeds (this is sometimes called eutrophication). If excessive growth occurs, or if the drinking water standards (45 ppm of nitrate) are exceeded, then nitrate must not be discharged. It may be possible to concentrate and cement nitrates. Nitrate can be destroyed by a sewage-type biological treatment specifically built for the purpose. The treatment is called "denitrification."

7.7 Solvent Extraction

Many organic chemicals in wastewater are more soluble in an organic solvent than in water. The ratio of solubilities is such that the concentration in the solvent may be 6 to 10 times the concentration in water if kerosene is used as a solvent, and may be 60 to 100 times for better solvents. (Methylisobutyl-ketone is a particularly good solvent.) To perform an extraction, a batch of wastewater is vigorously stirred with a volume of solvent which may be equal to the volume of the water or as little as one-tenth of the volume of the water. Stirring is then stopped and the solvent, which has a very low solubility in water, is allowed to float. The floating solvent is carefully drawn off. Often, to obtain more extraction, a second batch of fresh solvent is added to the tank and the procedure is repeated.

The solvent, contaminated with waste, may simply be burned as fuel in the incinerator. Or, the solvent may be recovered for reuse by distillation as described in Section 6 on Solvent Recovery. This also recovers the organic waste.

It is complicated to remove contaminants to very low levels. Also, some solvent always dissolves in the water. This process does not usually yield very clean water. Solvent extraction is best used to remove most, but not all, of contaminants which are very concentrated in wastewater (more than 5,000 to 10,000 ppm = 0.5 to one percent).

Quality of Treated Water

Solvent extraction removes more than 80 percent of the extractable compounds. The percent removed is increased by using repeated batches of clean solvent. The treated water is usually still high in extractable compounds and probably contains more than 100 ppm. Extraction always requires an additional treatment.

Emissions

The emission is a solution of waste in solvent which may be incinerated. If the waste and solvent are separated, the emissions described in Section 6 on Solvent Recovery will occur.

7.8 Steam Stripping

If wastewater is heated to its boiling point and then steam is forced through the water, a great many hazardous chemicals vaporize and leave in the steam. For the correct chemicals, it is reasonable to obtain a transfer of at least 99 percent of the chemical from the water to the steam.

A list of hazardous chemicals which can be most easily steam stripped is given in Table 7-3. Two properties combine to make a chemical easily removable by steam stripping; it should have a boiling temperature lower than water and have a very low solubility in water. Chemicals with a boiling temperature lower than water will prefer to be a vapor at the boiling temperature of water. Also, the fact that the chemical has a low solubility in water means that the water molecules are trying to push the other molecules out of the water; this also encourages vaporization. All the chemicals in Table 7-3 have low solubility in water, and most boil at temperatures below the boiling temperature of water.

TABLE 7-3 SOME TOXIC ORGANIC COMPOUNDS WHICH CAN EASILY BE STEAM STRIPPED

Benzene
Chlorobenzene
Dichlorobenzenes
Ethylbenzene
Toluene
Styrene
Xylenes
Most PCB's
Methyl chloride
Methylene chloride
Chloroform
Carbon Tetrachloride
Chloroethane
1,1-Dichloroethane
1,1,1-Trichloroethane
Hexachloroethane
Vinyl chloride
1,2-Dichloropropane
1,3-Dichloropropene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Methyl bromide
Dichlorofluoromethane
Trichlorofluoromethane
Dichloroethylenes
Trichloroethylene
Tetrachloroethylene
Allyl chloride
Toxaphene
Isoprene
Carbon disulfide
Cyclohexane

This process will remove only those organic compounds which are quite insoluble in water (usually less than 1,000 ppm) and have a low boiling temperature. In spite of its limited use, steam stripping can be valuable because:

(i) stripping removes volatile compounds that might be odorous or hazardous if passed on to the other treatments described in Section 7.

(ii) Many of the compounds that can be removed are toxic, and steam stripping can be used to concentrate them for incineration.

(iii) Steam stripping allows recovery of the compounds which may be reused.

(iv) Many of the compounds that can be removed are not destroyed in the general purpose biological oxidation treatment.

(v) Steam stripping can remove more than 99 percent of the selected compounds.

The hazardous chemical in the steam vapor is five to ten times more concentrated than in the original wastewater. The vapor can be incinerated to destroy the hazardous chemical. But recovery is also possible. If the vapor is condensed, there will be so much chemical compared to water that all of the chemical cannot dissolve and two separate liquids, one floating on the other, will appear. The upper layer will usually be mixed organic chemicals with very little water which can be sold or burned. The bottom layer will be water saturated with organic chemicals which can be put back into the steam stripper.

Quality of Treated Water

Stripping reduces strippable compounds by 99 to 99.9 percent. Since strippable compounds are usually insoluble and not present at more than about 1,000 ppm, treated water will usually contain 1 to 10 ppm remaining strippable compounds and may be fit for discharge if non-strippable compounds are not present.

Emissions

Emissions from steam stripping can include vapors which must be retained as described in Section 6 on Solvent Recovery, and cleaned water. Whether or not the water requires additional treatment before discharge will depend on the original composition of the wastewater and the vigor of the steam stripping.

7.9 Biological Oxidation

Biological oxidation is the process in which living organisms, mostly bacteria, cause the reaction of dissolved oxygen with dissolved and suspended organic molecules to make more organisms and small residual molecules, mostly carbon dioxide. Carbon dioxide escapes to the atmosphere. The result is water cleaned of most of the organic content and a settleable, separable sludge of dead and living bacteria. Very approximately, the organic carbon is about equally distributed between sludge and carbon dioxide.

Biological oxidation requires the presence of bacteria, organic matter and dissolved oxygen. For most wastes, the concentration of bacteria yielded by a once-through reactor is not high enough to obtain an adequate rate of reaction. It is usual, therefore, to separate the sludge from the slurry leaving the oxidation tank and return much of it to the tank. The balance of the sludge is disposed of. This maintains a high bacterial concentration in the reactor at all times. This procedure is called the "activated sludge" process. Another way to obtain high concentration of bacteria is to grow the bacteria on a solid surface and to pass the wastewater in a thin film over the surface. This is the principle of a "trickle filter."

The bacteria, or biological agents, occur naturally in soil, and once the biological oxidation treatment is established, the bacteria replenish themselves by growing on the waste. Replacement of bacteria is not needed.

Oxygen is supplied by air. Usually big stirrers are used in the oxidation basin to stir the water and draw air below the surface. Oxygen dissolves to make up the oxygen consumed in the breakdown of the organic waste. The stirrers are also necessary to keep the bacteria in suspension so they are uniformly distributed throughout the wastewater.

In the absence of oxygen, bacteria will convert organic matter to more bacteria and methane. This is called anaerobic treatment. It has the particular advantage of not requiring a large energy input for oxygenation or aeration. However, anaerobic treatment is a slow and unstable reaction, probably not suitable to a hazardous waste treatment facility.

An activated sludge biological oxidation treatment is a standard sewage plant. The process has been studied for more than half a century and a very large number of studies are going on today to further improve the process. Activated sludge is also the most widely used treatment for industrial wastewaters. For example, every paper mill has an activated sludge plant. However, for a hazardous waste treatment facility, biological oxidation has certain disadvantages, which mean that it will usually be used as a follow-on or second treatment, and not used alone.

Biological oxidation involves the action of bacteria which are living organisms. They flourish best when they are growing in a uniform environment. Changes in the type and concentration of the waste will upset the treatment and slow it down. In an extreme upset the bacteria may be killed. It will then be necessary to add fresh bacteria and slowly build up a large enough bacterial population so the plant is working smoothly. It takes from three to six weeks to start up most activated sludge plants and reach a peak rate of reaction. Compounds which can easily and rapidly be degraded when dilute will kill the bacteria if a batch of concentrated waste is suddenly put into the oxidation basin. Phenol is a typical example of a hazardous waste. It is very rapidly degraded if dilute,but kills the bacteria if the concentration suddenly jumps above about 500 ppm. Since the hazardous waste treatment plant will receive a varied waste, the incoming wastes will have to be stored, mixed and perhaps diluted before putting them into the biological oxidation. A treatment such as solvent extraction can be used ahead of biological oxidation to make the concentration going to biological treatment more uniform.

Some toxic chemicals are not decomposed by the natural bacteria in an activated sludge plant. Chlorinated compounds are examples of compounds that are poorly and slowly decomposed. If non-decomposable compounds (called biorefractory) are present in enough concentration, they may kill the bacteria. More usually they will pass through the biological oxidation unchanged. Biorefractory compounds must be separately removed either before or after biological treatment. Steam stripping and activated carbon are two methods of removing biorefractory compounds.

Hazardous, volatile chemicals must not be allowed to enter an activated sludge plant. The large volumes of air that are mixed into the water will sweep volatile compounds out of the water into the atmosphere. All hazardous volatile compounds must be steam stripped in advance if biological oxidation is to be used.

Quality of Treated Water

Experience with industrial activated sludge plants is that the biochemical oxygen demand (BOD) in the treated water is reduced to 10 to 30 ppm. That is, the carbon in the treated water will be in the range of 2 to 10 ppm and will be fit for discharge if the carbon does not come from highly toxic compounds.

Emissions

If vapor emissions are controlled by pretreatment, the remaining emission is the surplus biological sludge. Most of this sludge is dead and living bacteria. However, undecomposed waste molecules are adsorbed onto the sludge and may render the sludge hazardous. A facility specializing in hazardous waste must not use the sludge for landfill and soil conditioning as is done by sewage plants. The sludge should be incinerated.

7.10 Carbon Adsorption

Charcoal can be activated by heating it in steam with so little oxygen that the carbon does not all burn away. Wood charcoal, coconut shells, coke, petroleum coke and other charcoals can be activated. An activated carbon particle has a very large surface area like a sponge and a strong ability to adsorb organic chemicals onto the surface. Lumps of activated carbon are packed into a bed and wastewater is allowed to trickle through the bed. The wastewater spends several seconds in the bed and organic contaminants are pulled out of the water and stick to the surface of the carbon.

Activated carbon is the single, most universally applicable wastewater treatment. Most chemicals stick so strongly to the carbon that they can be removed from the water to very low concentrations (single number parts per million and below). Thus, activated carbon is particularly suitable for dilute wastewaters. Activated carbon will usually follow other treatments including biological oxidation. However, activated carbon may be used to remove hazardous chemicals in higher concentrations if they are not biodegradable. For this purpose activated carbon is often added to the biological treatment basin.

Once the surface of the carbon is covered with organic molecules, it can adsorb no more and is no longer active. Since carbon has a limited capacity it will be used on wastes that are as dilute as possible.

Quality of Treated Water

Table 7-4 shows the residual after activated carbon treatment for selected hazardous compounds as given in the EPA "Treatability Manual" Vol. III. Of 112 toxic organic compounds listed in the manual, carbon adsorption is highly efficient for 59, of low efficiency for 14 and either of medium efficiency or unknown efficiency for the rest. Water, after treatment, is usually fit for discharge.

TABLE 7-4 RESIDUAL AFTER ACTIVATED CARBON

Compound	Residual* (ppm)	Compound	Residual (ppm)
Phenol	0.0007	Chloroform	BDL
Benzene	0.005	Trichloroethanes	BDL
Chloroethane	2.5	Vinyl Chloride	8.6
Dichloroethanes	0.09 to BDL		
Methylene Chloride	0.019		

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*Median Values

BDL = Below detection limit

Emissions

The emission is used carbon. This can easily be incinerated. However, it may pay to reactivate it. Much fuel is expended to make steam to activate carbon, and if the carbon is incinerated after one use this fuel is wasted. Used carbon can be steamed and reactivated. Total reactivation is not possible; some carbon oxidizes and some activity is lost. But from 50 to 90 percent of the activity can be restored. Reactivation produces a vapor emission which will probably be hazardous and must be incinerated.

7.11 Summary of Emissions from Water Treatment

7.11.1 Vapors

It is important that wastewaters sent for treatment not release hazardous or odorous vapors. In a biological oxidation plant using air to supply oxygen, it is not possible to contain vapors. For most of the other treatments described (precipitation of metals, desalination, oil separation, solvent extraction and carbon adsorption) containment of vapors requires unusual equipment. The best procedure is to strip all waters which release vapors before any other treatment. Steam stripping equipment is specifically designed to contain vapors by condensation and incineration. The heat applied in steam stripping will break oil emulsions, and all other treatments that may follow stripping will be done on colder water than stripping. The lower temperature ensures that vapors will not be emitted.

If activated carbon is regenerated, the vapors will have to be contained.

7.11.2 Sludges and Solids

Metal precipitation leaves a sludge which must be stabilized and landfilled.

Biological oxidation leaves a sludge which should be incinerated.

Oil separation may leave a sludge which should be incinerated.

Used carbon can be incinerated.

7.11.3 Liquids

Oil separation, steam stripping and solvent extraction will produce an organic liquid that can be used or incinerated. The liquids must be handled and transported with the same precautions used in the original manufacturing plants.

Desalination gives a concentrated solution of calcium chloride which must be safely removed for use or disposal elsewhere.

7.12 Performance and Reliability

Carbon adsorption is a well established and reliable process that has been used for many years. It is, however, necessary to ensure that the carbon is not saturated.

Precipitation of metals is well established. It is a batch treatment that is reliable if the sequence of operations is carried out carefully and enough time is allowed.

Desalination processes, particularly evaporation, are also reliable.

Biological oxidation of hazardous wastes is not well tested. Careful monitoring is essential and upsets can occur.

Steam stripping requires careful monitoring. Each waste will behave differently.

Solvent extraction is specific to each waste and each solvent. Laboratory tests will be required before using this treatment. The results must be carefully monitored.

7.13 Monitoring and Disposal of Treated Water

Treated waters must be held in batches for monitoring before reuse. Monitoring of treated water differs from the monitoring of incineration gases in several important respects. First, it is not possible to hold incinerator gases in batches for analysis before release. It is possible to hold treated water in batches and to retreat a batch if it is found to be contaminated.

Second, continuous analysis of incinerator gases, while difficult, is easier than continuous analysis of water. This is mostly because the types of chemicals requiring analysis in incinerator gases are fewer than the types of chemicals requiring analysis in water.

Third, when incinerator gas is found to be contaminated, the incineration conditions can be quickly changed to remedy the problem. A few minutes may suffice. Changes in most of the water treatments take hours.

Fourth, incineration is continuous over a period of hours or days. For as long as the particular waste being burned is available with no change in feed material or incineration conditions, sudden changes in gas composition are unlikely. On the other hand, most water treatments are carried out on discrete batches of wastewater and the results can vary from batch to batch.

For the reasons given, treated water must be held in batches and analyzed in the laboratory before release. Water with an unsatisfactory analysis must be retreated. The storage basins can be concrete or other impermeable material, but need not usually be covered.

7.13.1 The Consequence of Failure

If a batch of treated water is found to be unsatisfactory, it will be retreated.

7.14 Summary of Recommendations for Disposal of Treated Wastewater

Any wastewater can be detoxified provided it is treated appropriately. The most difficult aspect of treating hazardous wastewater is to choose the treatment. To this end we make the following recommendations:

Choose the Correct Treatment

Install the best analytical equipment and be sure the person using it is fully trained.

Segregate and analyze all incoming wastewaters and wastewaters produced by other treatments. Analytical procedures must be established and followed. Wastewaters received for the first time should probably be checked for all the chemicals on the EPA priority pollutant list. When a wastewater is received repeatedly from the same source occasional batches should be checked for priority pollutants.

For each separate batch of wastewater choose the correct treatments. If required, carry out laboratory tests to determine the conditions for the treatment.

Monitoring

Segregate and analyze all treated waters for the pollutants which were found in the untreated wastewater.

Action

Retreat waters found to be unfit for discharge.

Agreement

An agreement should be made between the operator of the facility and the town, as to what is permitted and what is not permitted in water discharged to a local sewer or river.

One way to ensure that toxic chemicals are not released, is to put into the agreement that the treatment facility will be governed by the discharge regulations for each separate industry, sending wastewater to the facility, as well by the regulations governing a treatment facility. This means that chemicals on the EPA priority pollutant list cannot be discharged in dangerous quantities.

Discharge of chemicals which are not toxic should also be limited by agreement. Limits should be placed on oxygen demand, turbidity, nitrogen and chloride. The limits should depend on the use to which the receiving river is put, for example drinking water, recreation, fish growth, etc.

8. STABILIZATION AND DISPOSAL OF NON-COMBUSTIBLE SOLIDS

8. STABILIZATION AND DISPOSAL OF NON-COMBUSTIBLE SOLIDS

8.1 Introduction

The facility will have to deal with an important quantity of non-combustible waste which may be dry or in the form of a concentrated sludge or slurry in water. Some of these wastes have passed through, or resulted from, other treatments within the facility. Non-combustible solids leaving the rotary kiln section of the incinerator are one example. Other examples are solid material that settles out of the incinerator scrubbing water, and metal precipitates from the wastewater treatment section of the facility. It may also be necessary to deal with chloride solutions made by concentrating the incinerator scrubber water or incoming wastewater which has been neutralized in the plant.

In addition, the facility will most probably receive hazardous sludges specifically for treatment and disposal. A most important example is sludges from in-house wastewater treatment in metal finishing and electro-plating shops.

All treatments of non-combustible waste are intended to chemically fix or stabilize the waste so that it is insoluble. It is necessary that non-combustible waste be left on or in the ground and it must not dissolve, or leach, into rain water.

Stabilization treatments are described in the next section. Just as wastewater must be held and analyzed after treatment and only released if it is non-hazardous, treated solids must be held and analyzed after stabilization and only released if they are truly stabilized. The test for adequate stabilization is that the solid does not leach when put into the ground. Laboratory tests for leaching are not adequate and the only way to determine if stabilization is complete is to check for "real life" leaching by rain when the solid is put into a pit in the ground.

It takes up to a year to determine that a treated solid waste is not leaching. The full determination is best made through all the seasons of the year. Thus the treated solid sits in a pit in the ground for a year. This pit must be lined with impermeable material to insure that if, by accident, stabilization is incomplete, leached materials do not sink into the groundwater. A lined pit is called a "secure landfill". During the year of testing, the rain water inside the pit must be analyzed for materials that may be leaching from the solid. The rainwater from inside the pit, if found to be hazardous, must be pumped out and treated. If, at the end of a year of testing the rain water inside the pit is found to be leaching solids, then all the solids must be dug out, retreated, and held for retesting.

In addition to all the monitoring inside the secure landfill, the groundwater outside and below the landfill must be monitored according to law to ensure that the pit lining is not leaking. If the pit lining is leaking hazardous materials, the contents of the pit must be dug out and retreated. The construction and monitoring of a secure landfill is described in a later section.

We emphasize that the treatment and disposal recommended here and proposed by IT Corporation in their Notice of Intent is not the procedure usually followed, but is very much better. Most secured landfills today are used to store untreated or unstabilized waste for an indefinite time. This is why the laws about monitoring the groundwater are so important. Most stabilized waste is put into an ordinary fill and not into a secured landfill. Thus most stabilized waste is dumped without testing the adequacy of the stabilization. If all waste is stabilized and held for a year in a secure landfill and then found not to be leaching the possibility of harm in the distant future should be very low.

At the end of the year the stabilized waste may be dug up and used for ordinary landfill such as a road bed, or it may be covered and left where it is. If the waste is left where it is, the monitoring wells must be left in place and monitoring must continue, but infrequently, probably annually.

8.2 Stabilization

The state-of-the-art was summarized in 1979 by the U.S. Army Engineer Corps (Reference 7). The techniques shown in Reference 7 to be well established are summarized here, with the information supplied by the companies. Stabilization is most suitable for toxic metals. Small quantities of organic waste will be stabilized, but for larger amounts the results are variable. In Massachusetts, any waste with more than small amounts of organics must be incinerated and only the ash (or non-combustibles) from the incinerator will be stabilized and landfilled. So-called polyvalent metals are stabilized. Monovalent metals, in particular sodium, are not stabilized, but monovalent metals are not toxic. Also, the second part of the salt, called the anion, is not easily stabilized. Chloride is not easy to stabilize. Cyanide is not stabilized and must be destroyed.

8.2.1 Cement

Common cement or "portland cement" is made by heating a mixture of limestone and clay (or similar materials) at a high temperature for a long time in a rotary kiln. The limestone (calcium carbonate) decomposes to lime (calcium oxide) and the lime reacts with the silicates in the clay to form complex silicates of calcium. Compounds of calcium and aluminum (aluminates) are also formed. The entire mass partly fuses and leaves the kiln as a clinker. When this clinker is ground fine it is portland cement.

When cement is stirred with water it chemically reacts with the water (it "hydrates") forming interlacing, thin, densely-packed, fiberlike crystals of silicates which set to a dense mass. For construction purposes, sand and gravel are mixed with the cement and water. The cement mass surrounds the particles of sand and gravel which serve to make the hardened block stronger than if only cement were used. Metal oxides and hydroxides in precipitated sludges will similarly be surrounded and locked-in by the cement as it hardens.

Cement, as a stabilizing agent, has the advantages of being available everywhere and being easy to mix. Workers need not be specially trained. Wet sludges are stabilized directly because water enters into the chemical reaction; drying is not needed.

Cement will stabilize chlorides to a large degree. For example, cement can be prepared and hardened when slurried with sea water. A solution of calcium chloride can also be solidified in cement.

The disadvantages of using cement are:

(1) A large mass of cement is required. The weight and volume of the final product is usually about double that of other fixation processes.

(2) If sulfates are present in the waste, and they often will be present, a special grade of cement is required. Not all grades of cement will harden in the presence of sulfate. The special cement is obtainable, but one must be certain to use it and not the common grade.

(3) Metals in solution have been found, in some cases, to not be as perfectly stabilized as is required. Only precipitated metals will be stabilized in a hazardous waste facility, so adequate stabilization is expected from cement.

8.2.2 Other Cement-Like Materials

Other cement-like materials will be briefly mentioned. Their major advantage over cement is that they are cheaper and smaller quantities are required.

The most common materials that will harden like cement are flyash produced when coal is burned in an electric generating station, and ground blast-furnace slag from steel making and cement-kiln dust. These materials require lime for the hardening process. The processes sold by Dravo Lime Company in Pittsburgh, PA., and by I.U. Conversion Systems in Horsham, PA., probably use some of the cement-like materials described.

8.2.3 Chemical Fixation Processes

The use of more refined silicate binders has two advantages over cement.

(1) The metals that need stabilization are converted to silicates which are particularly insoluble. Leaching has been found to be undectable.

(2) The final, stabilized mass and volume are only about 5 percent to 15 percent higher than the mass and volume of the unstabilized waste.

Fixation is the most probable type of process for use in a hazardous waste treatment facility. One process is sold by Stablex Corp. in Radnor, PA. The stabilized material hardens in the landfill and can be used, for example, in road beds.

Another process is sold by Chemfix in Kenner, LA. Their stabilized material looks like a synthetic clay. It is crumbly and can be moved with earth moving machinery. The color varies with the waste and may be black or somewhat red. The stabilized waste can be compacted and will be load bearing in the same way as most earth is load bearing.

Canadian Waste Technology in Toronto, Ontario, emphasizes that they can use a wide variety of silicates to do the fixation and that their stabilized material is essentially the same as earth (not topsoil, but the natural silicate earths found below the topsoil). This firm states that chloride can be stabilized if not present in wastes in too high a proportion.

8.2.4 Encapsulation

Encapsulation will probably not be used in a hazardous waste facility. It is unnecessary. The waste crystals are finely ground and each crystal is coated with asphalt in special mixing machinery. The mixing is done hot and all water boils off. The molten asphalt is then cast into shapes for landfill. This is an expensive process using special machinery on which operators must be specially trained. Energy is required to boil off all the water. Werner and Pfleiderer Corp. in Ramsey, N.J. sell the equipment and a process. They have extensive European experience.

8.2.5 Emissions and the Consequence of Failure

Emissions will not occur from fixation. Only wastes that do not vaporize will be fixed. Usually the water in sludges will be fixed. If there is too much water and some concentration of the solid is required (by settling, pressing or filtering), the surplus water must be contained and sent to water treatment.

If a waste were truly stabilized, it could be used for ordinary landfill and construction. However, it requires a long time to discover whether stabilization is complete. For this reason stabilized waste in a hazardous waste treatment facility must be put into a "secure" landfill instead of an ordinary landfill. The secure landfill allows the opportunity to discover whether stabilization is complete and to correct the stabilization if it is not complete.

8.3 Secure Landfill

8.3.1 Secure Landfill

A diagram of a secure landfill with monitoring points is shown in Figure 8-1. A secure landfill is a sealed pit whose base is above the water table. By law the sealant must be at least 3 feet of clay whose natural permeability is 10^{-7} cm/sec; sheets of rubber or plastic may be

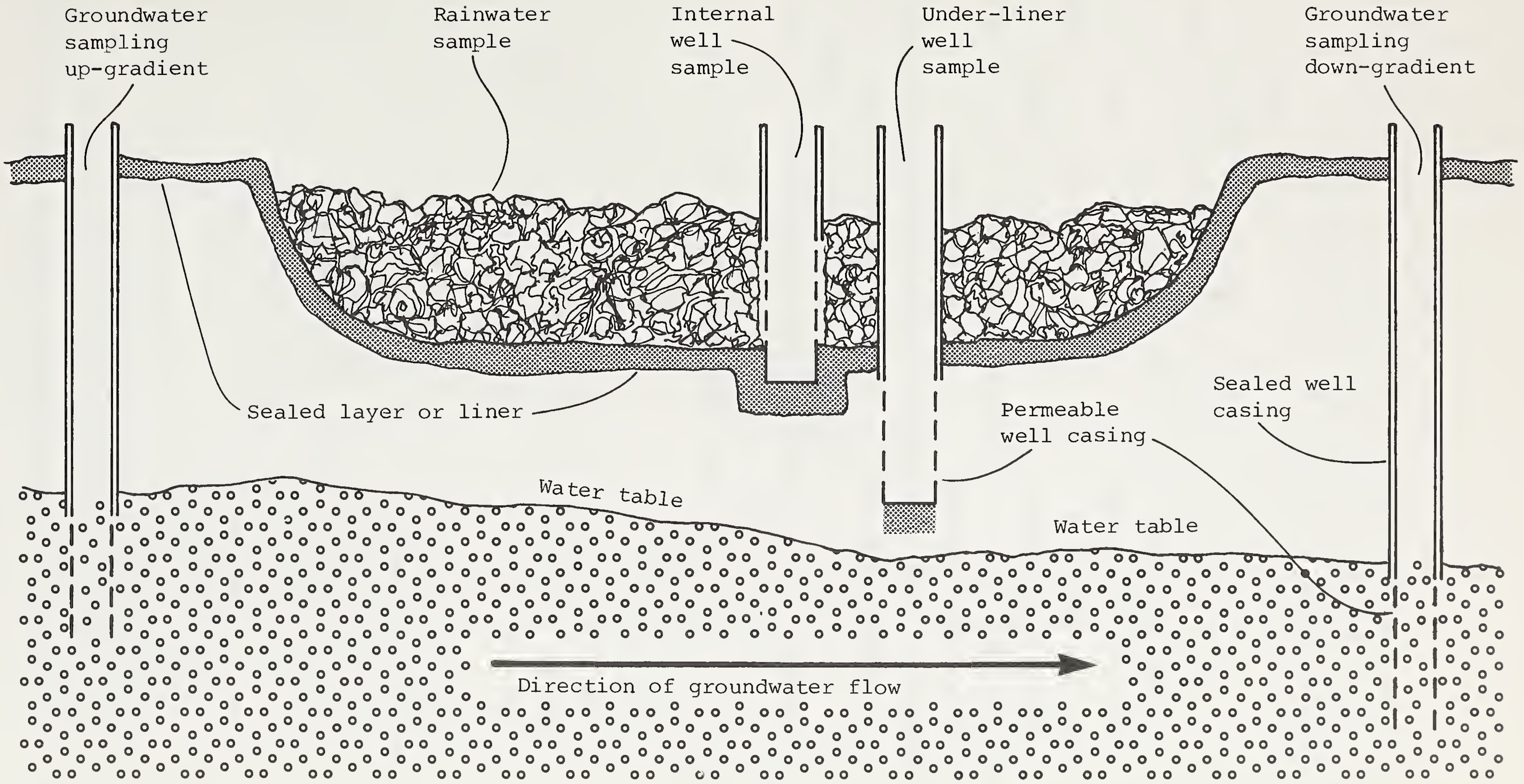

Figure 8-1. Diagram of an open secure landfill.

used if they also conform to the law. In addition, free board must be available above the filled material to contain the largest rain storm to fall in a 24-hour period over the previous 10 or 25 years. Finally, a secure landfill must be monitored as discussed below.

A landfill will normally be big enough to contain a one-year production of stabilized waste, not more. Rain will accumulate in an open landfill pit. The rain must be sampled and analyzed at regular intervals of about one week to one month. As the pit fills, some of the accumulated rain must be pumped out. Pumping will be necessary if the level of water gets too close to the top and before the pit is finally sealed off. When water is pumped out of the landfill the water must be analyzed and treated as required before discharging. The "internal well" (see Section 8.3.2. below) is used for pumping.

At the end of about one year when the pit is filled with stabilized waste, if it is found that leaching is not occurring, the pit will be sealed with clay and covered with earth. The top layer of earth will be seeded or will naturally grow grass and other vegetation so it will not be unsightly and will not erode.

When one pit or cell is closed a new pit or cell will be prepared and used for the next year.

8.3.2 Monitoring

A secure landfill must be monitored. By law samples must be taken from the groundwater and analyzed to determine if any hazardous materials have been added to the groundwater. As shown in Figure 8-1, wells are drilled to below the water table. They are securely cased above the water table and are open within the water. Thus, the samples taken through the wells are samples of groundwater and not the result of percolating rainfall. At least one well must be placed up-gradient (or up-stream) relative to the movement of groundwater, to give a true analysis of natural groundwater. At least three wells must be placed down-gradient to search for any possible contamination.

Samples taken from the wells must be analyzed for metals. In addition, a simple total carbon (or similar) analysis will be made to determine if the organic content of the water has changed.

The groundwater monitoring wells will only show contamination if the fill in the pit has not been adequately stabilized and if the pit liner is leaking. For a landfill of the type recommended here, which receives only stabilized waste to be held for testing, the groundwater monitoring wells are simply a final precaution. They are not the main control mechanism.

Two other wells are shown on Figure 8-1. The "internal well" is sealed at the surface of the ground and open within the fill. Samples taken from this well are the result of rain water percolating through the fill. This well is the main control point. It is used to check the adequacy of the stabilization treatment. It is quite possible that fill may leach for a few months when it is first put into the pit. After a while any metals left on the surface of the stabilized solid have leached off and leaching stops. This is not a problem and is the reason for putting the stabilized solid into a secure landfill. When the samples from the internal well are found to be hazardous the water must be pumped out through the well and treated.

Also shown on Figure 8-1 is an "external well." The external well is not required by law but may be used. This well is cased to below the pit and then open. It is placed below the lowest point of the pit and can serve to obtain advanced warning that the pit sealer is leaking. This well cannot give advanced warning of all leaks but will give warning of leaks near the lowest point of the pit. The warning will be in advance of detecting hazard in the groundwater. If hazardous chemicals are leaking, the landfill must be dug out and moved to another freshly lined pit.

8.4 Summary of Recommendations for Disposal of Non-combustible Solids

The procedure recommended in this section is summarized as follows.

Procedure

Chemically stabilize all non-combustible waste stored on-site.

Hold stabilized waste for a period of about one year to check that stabilization is complete. Hold in a secured landfill or pit.

Monitoring

Monitor rain water inside the pit for leached hazardous materials.

Monitor groundwater outside the pit for leaking hazardous materials.

Action

Pump water out of the pit and treat before discharge if the water contains hazardous materials.

Dig up the fill and restabilize if leaching is occurring at the end of the test period.

Transfer the fill to a new pit if the pit liner is found to be leaking hazardous materials.

9. EMISSION OF HEAT AND CONSUMPTION OF WATER

9. EMISSION OF HEAT AND CONSUMPTION OF WATER

A typical incinerator burns waste fuel at a rated 90 million Btu per hour. This heat will be used as much as possible and the remainder will be released to the atmosphere at as low a temperature as possible.

Ninety million Btu is the heat obtained by burning about 650 gallons of fuel oil. A four bedroom house may need about 1,100 gallons of fuel oil in a year, so the incinerator gives heat equivalent to about 5,000, 4-bedroom houses. When fuel oil is burned in a house, the high temperature heat of the flame is transferred to lower temperature heat in steam, hot water or hot air. Next the heat is transferred to a still lower house temperature. Finally the heat is released to the atmosphere by leaking air and by passage through walls and closed windows. By the time the heat is released its temperature is 20° to 40°F above the atmosphere, which is so close to atmospheric temperature that no further use can be made of it. The heat is now called "waste heat."

To determine the effect that the incinerator heat has on the atmosphere, we will follow the heat as it is used or passes through various processes and becomes lower and lower in temperature. The discussion is given in the next subsection. There are several paths which the heat travels and the description is necessarily complicated. Figure 9-1 serves as a map, and the results are summarized in two subsections later.

9.1 Distribution of Incinerator Heat

A small amount of heat, about 2 million Btu/hr, is lost directly from the incinerator walls to the air. Although the incinerator walls are well insulated, the outside surface will be about 40° to 60°F hotter than the atmosphere and heat will, therefore, be lost.

Most of the incinerator heat goes into hot combustion gases at about $1,800^{\circ}$F ($1,000^{\circ}$C). It may be used, and probably will be used, to produce steam. This will cool the gas to somewhere between 900° and 300°F. For an example we will assume that making steam cools the gas to 600°F. About 60 million Btu/hr will go to produce about 60,000 lbs of steam/hour. Later we will see what happens to the heat in the steam but first we follow the gas. The gas is next scrubbed with water.

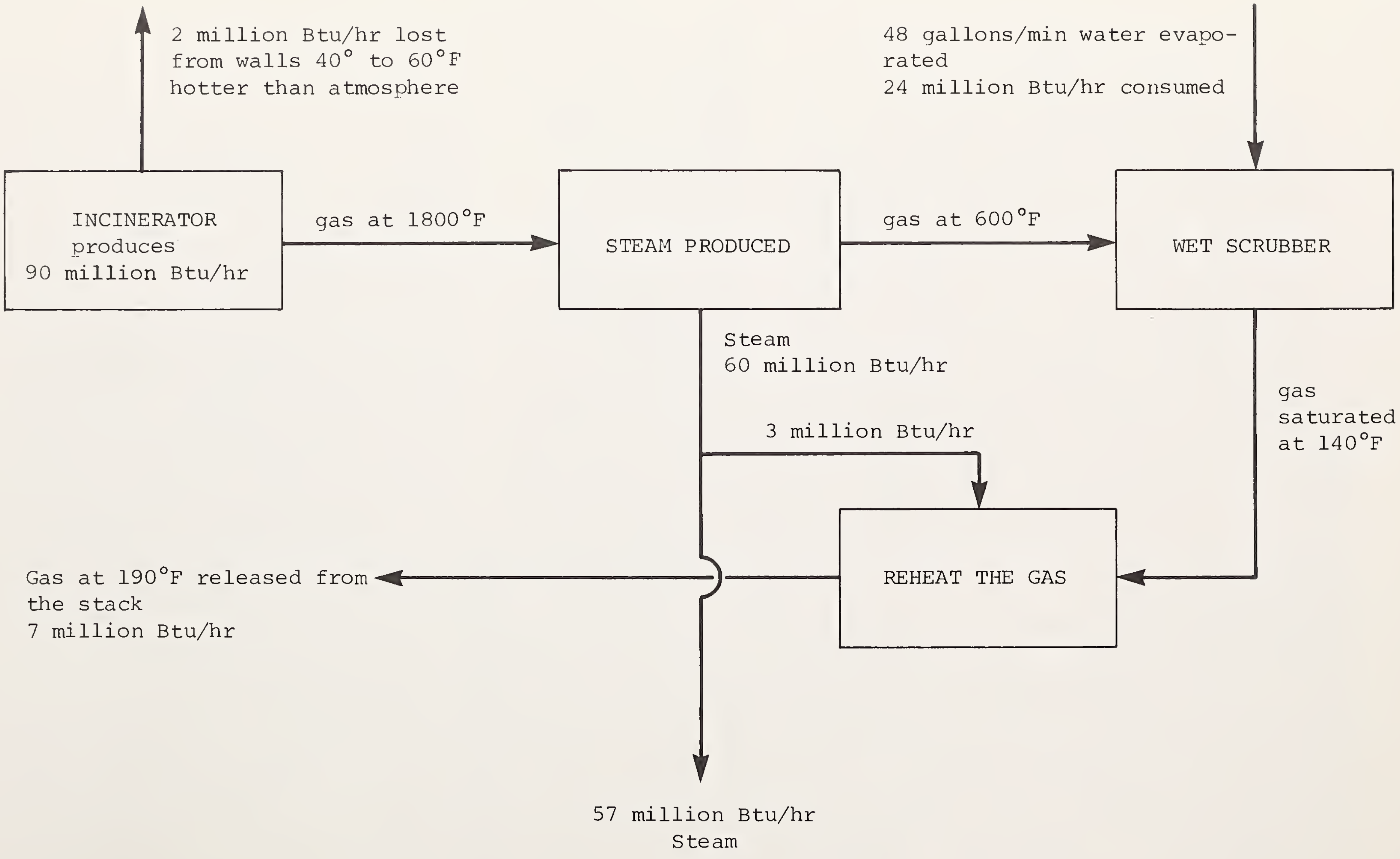

Figure 9-1. Distribution of heat from an incinerator when steam is produced for use.

When a hot gas is scrubbed with water, water evaporates. The heat needed to evaporate water is supplied by cooling the gas. The gas is cooled and water is evaporated. At the temperature finally reached the gas is saturated (that is, at 100 percent relative humidity). Calculations are approximate because we do not know how much water was put into the incinerator with the waste (we have assumed 18 gals/min from the waste, as shown in Section 5.5.2.). Since about 150,000 lb/hr of stack gas are released from the incinerator (this was calculated in Section 5.5.2.) we estimate that:

> if steam is not made and gas at 1,800°F is scrubbed, the scrubbed gas is cooled to about 170°F and about 80,000 lb/hr (160 gals/min) water are evaporated;
>
> if steam is made and gas at 600°F is scrubbed, the scrubbed gas is cooled to about 140°F and about 24,000 lb/hr (48 gals/min) water are evaporated.

On Figure 9-1 is shown only the case when steam is produced. Some of the steam (3 million Btu/hr) is used to reheat the scrubbed gas so it will rise from the stack. The reheated gas goes out to the atmosphere at about 190°F, taking with it about 6 million Btu/hr.

Some of the scrubber water is released, hot, to water treatment, carrying with it a very small amount of heat in the range of 0.3 to 0.5 million Btu/hr. (The calculation was made assuming 3 percent chlorine in the waste fed to the incinerator and 1 percent calcium chloride in the water released. Water is released at about 5,000 lb/hr (= 10 gals/min).) We emphasize that this water is held for analysis and possible treatment; it is not released to the river when hot.

There remains about 57 million Btu/hr in the form of steam. There are several possible uses and disposals for steam, which are summarized below:

1) The steam may not be needed at a particular time and only enough steam to reheat the stack gas may be produced. In this case, additional water will be evaporated in the wet scrubber and the stack gas will leave at a higher temperature. The values are given on Figure 9-2.

2) The steam may not be needed but may be produced. The un-needed steam must be condensed and the water returned to the boiler section of

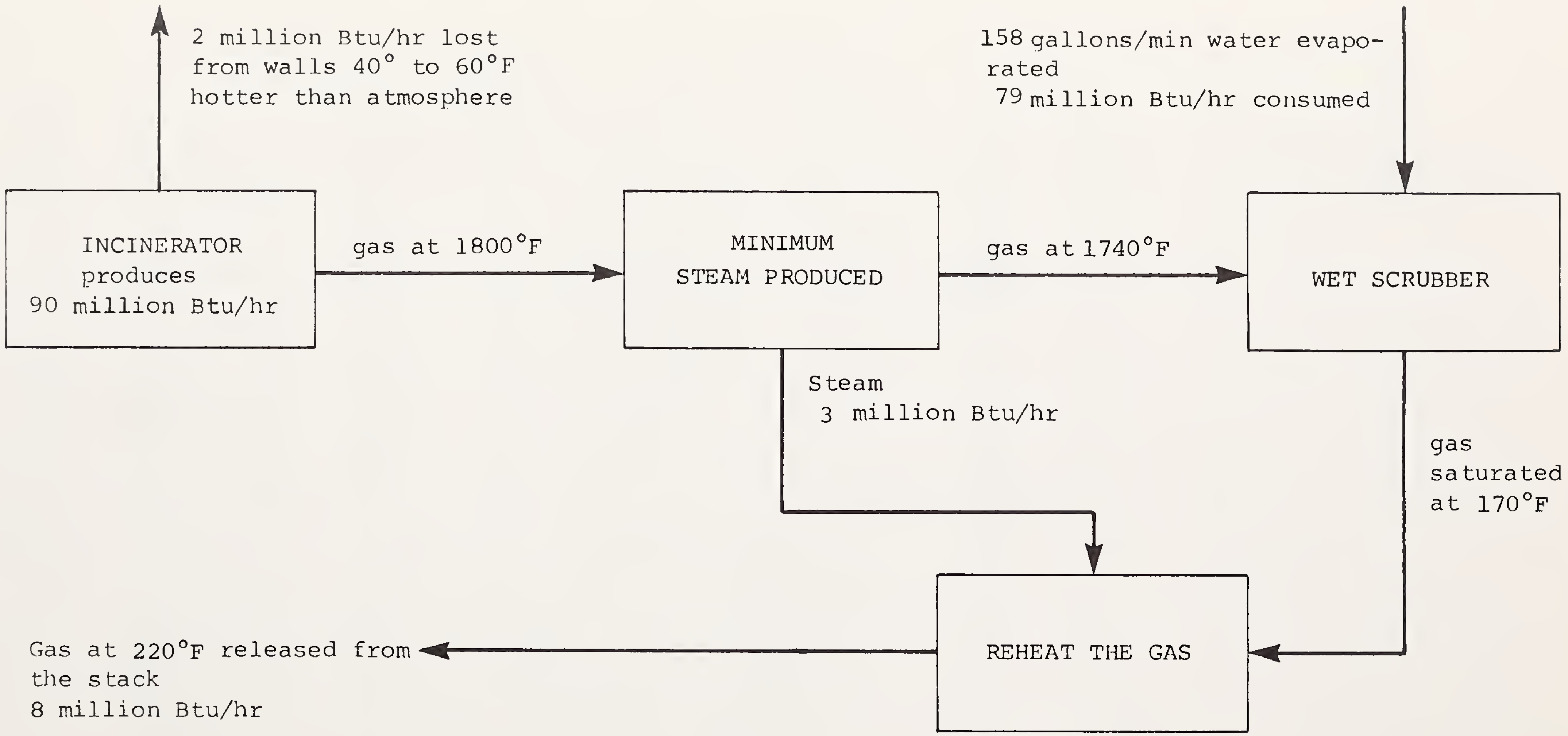

Figure 9-2. Distribution of heat from an incinerator when minimum steam is produced.

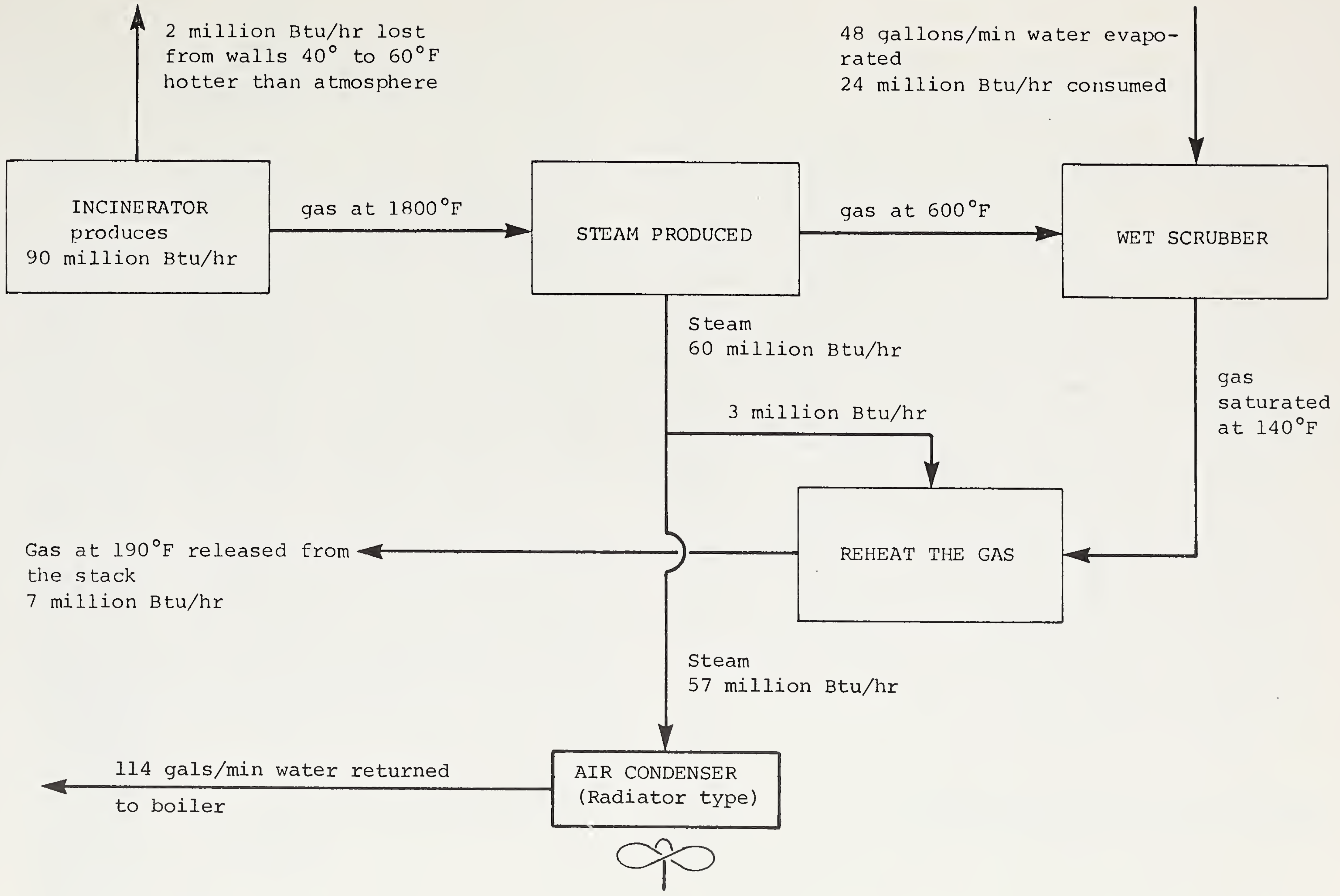

Figure 9-3. Distribution of heat from an incinerator when steam is produced, but is not needed.

the incinerator. The best piece of equipment for this is a device similar to an automobile radiator. Air is driven by a fan over a radiator. This cools the radiator and condenses the stream. The values are given in Figure 9-3.

3) The steam may be used in the solvent recovery still described in Section 6. As the steam condenses, organic solvent boils. The solvent is condensed at the top of the distillation column by cooling water. The cooling water is usually drawn from a local river and returned to the river. In this case, the heat ultimately is distributed to the ground and atmosphere and very little water evaporates or is consumed. The values are given on Figure 9-4. Alternatively, cooling water may be circulated through a cooling tower where some water is evaporated to cool the rest of the water. The disadvantage of a cooling tower in Massachusetts is that it is difficult to prevent fog from forming in winter.

Several possibilities have been given and all may be used at different times depending on the needs of the plant. The conclusions are summarized below.

9.2 Summary of Emissions of Heat

The most likely disposal of 90 million Btu/hr of heat is as follows:

1. Between 48 and 158 gals/min of water will be evaporated in the wet scrubber and released to the atmosphere as a gas.
2. Stack gas at between 190° and 220°F will leave the top of the tall stack and be dispersed.
3. Between zero and 37,000 gals/min of flowing river water will be heated by not more than 3.5°F.

9.3 Summary of Water Consumption

Water is only consumed if it is evaporated and sent into the atmosphere as a vapor. The point of consumption of water is the wet scrubber and between 48 and 158 gal/min of water will be consumed depending on how much steam is being made.

9.4 Recommendations for Emission of Heat

Unless the stack gas from an incinerator is reheated after wet scrubbing, it will be saturated. When saturated stack gas is released,

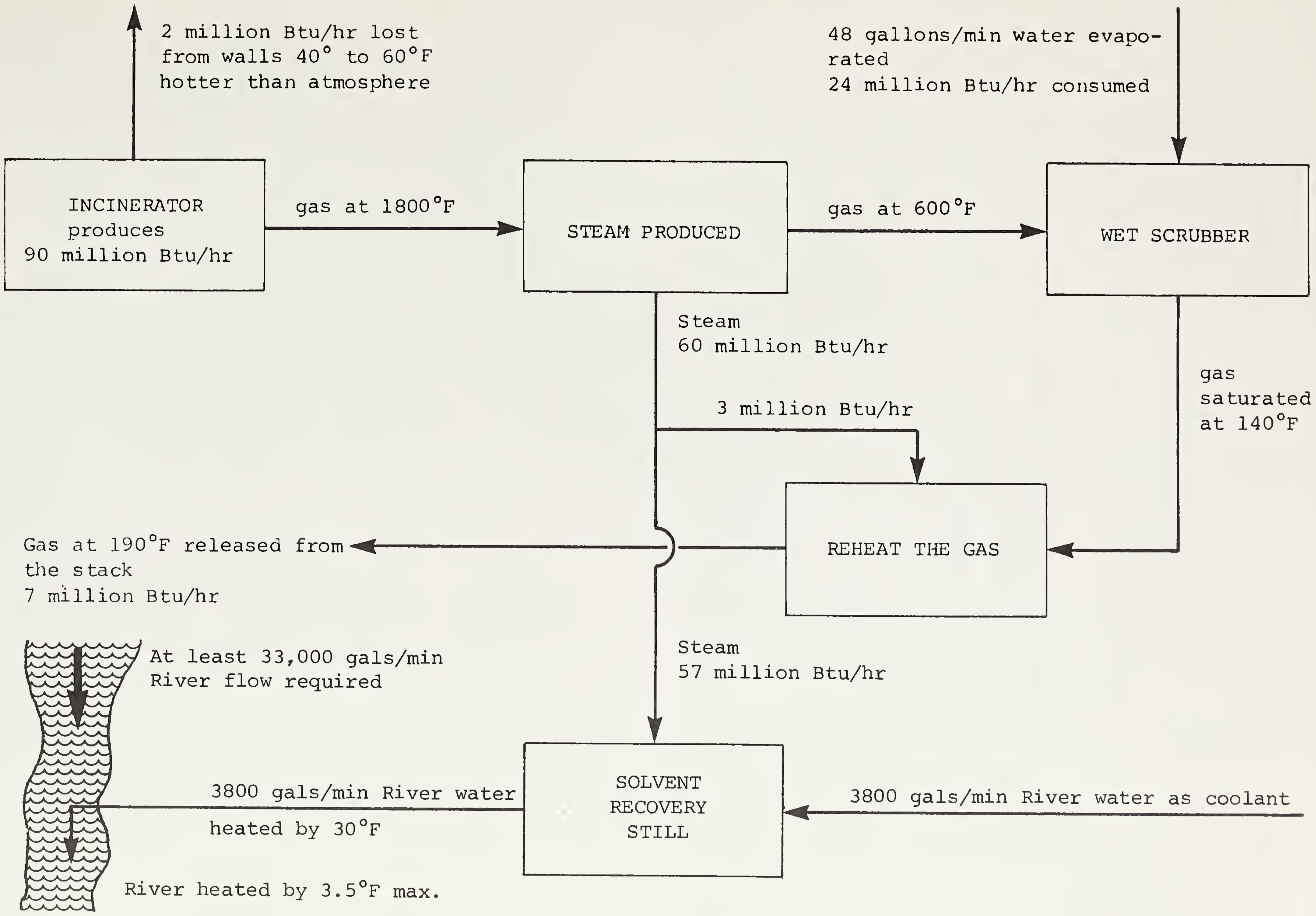

Figure 9-4. Distribution of heat from an incinerator when steam is produced, and used in a sovent recovery still.

water droplets will form because the gas cools as it comes into contact with the atmosphere. A visible plume will occur which may rise or descend, depending on local atmospheric conditions at any time. A visible plume is not harmful as long as it rises, but may be considered unsightly. A descending plume will cause fog in the summer and ice in the winter.

Both the visibility of the plume and the number of hours a year when the plume tends to descend can be controlled by designing the stack for local conditions and by reheating the gas. Stack design includes the height, the diameter and the use of a cone at the top of the stack.

The agreement between the operator of the facility and the town should make specific reference to the design of the planned stack and the degrees of reheat planned, if any. The operator of the facility should be asked to prove that it has been designed to minimize the visibility of the plume and, in particular, the number of hours per year when the plume is likely to descend.

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10. REFERENCES

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